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June 24-27, 2013,

Burduguz village, Irkutsk Region, Russia

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Boreskov Institute of Catalysis SB RAS, Russia
Max Planck Institute for Chemical Energy Conversion, Germany

Third Russian-German Seminar on Catalysis

Bridging the Gap between Model and Real Catalysis. Energy-Related Catalysis

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ABSTRACTS

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Сборник включает тезисы пленарных лекций и устных докладов секций: Получение чистого топлива; Производство и хранение водорода; Электрокатализ для топливных элементов; Хранение и преобразование энергии.

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PLENARY LECTURES

PL-1 ÷ PL6

Production and Storage of Hydrogen Using Catalytic Approaches

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The lecture summarizes two inter-linked areas related to hydrogen:

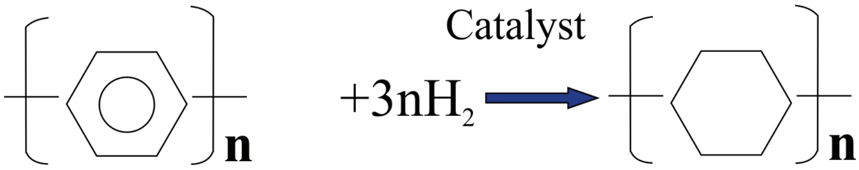
- Its production, especially from renewable materials, and
- Hydrogen storage

The economics based on the wide use of hydrogen is the destiny of the humanity, no matter how fast this period will come. We must be prepared to produce hydrogen in huge amounts, to transport it (even over huge distances, like from other planets) and to store it with a minimum consumption of energy. Presently the production of hydrogen is based on electrolysis of water or on oil and gas raw materials. Hydrogen produced from oil is used on site for the needs of the refinery producing hydrogen for hydroprocessing. Hydrogen produced from water is still very expensive and energy consuming. New competitive processes, probably related to the carbon trade, should become a real alternative to the old technologies. Natural gas (also, gas hydrates in the future) can be rationally converted into hydrogen by any of the three processes:

- Steam reforming $CH_4 + H_2O = CO + 3H_2$,
- Carbon-dioxide reforming $CH_4 + CO_2 = 2CO + 2H_2$,
- Partial oxidation $2CH_4 + O_2 = 2CO + 4H_2$

Advantages and drawback of each of these processes are considered from the point of view of energy consumption, safety and other aspects. The focus in the talk will be placed on the use of structured catalysts for the partial methane oxidation.

Hydrogen storage can be accomplished by either physical or adsorption or chemical methods of storage. The benefits of the chemical storage in combination with physical and adsorption systems are considered from the point of view of safety, hydrogen and energy gravimetric and volumetric capacity characteristics. The use of the composite catalytic materials based on reversible processes of hydrogenation of aromatic substrates (hydrogen accumulation) and dehydrogenation (hydrogen release) is given the prime attention, as well as to the novel Metal Organic Framework (MOF) materials usable as adsorbents and catalyst carriers.



PL-2

Carbon Nanotubes - Catalytic Growth, Functionalization and Applications in Electrocatalysis and Heterogeneous Catalysis

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Carbon nanotubes (CNTs) are promising materials for numerous applications because of their unique mechanical, chemical, and electrochemical properties. Due to their high aspect ratio, carbon nanotubes have a high tendency to agglomerate, and macroscopically, they are a dust-like material which is difficult to handle. In several recent studies the successful anchoring of this one-dimensional nanomaterial as branches to macroscopic supports has been reported, thus extending its applicability. In addition, specific surface modifications are often needed to improve the performance of CNTs in electrochemical and catalytic processes. Electrocatalytic processes have attracted much attention recently due to the revival of the fuel cell. At present, the electrolysis of water to generate hydrogen is discussed as possible route for storing solar energy harvested by solar cells. In chlorine industry, the recovery of chlorine from electrolysis of aqueous HCl can be achieved by replacing the traditional hydrogen-evolving cathode by an oxygen-consuming cathode, a so called "oxygen-depolarized cathode" (ODC). However, the oxygen reduction reaction (ORR) remains a major challenge in basic as well as applied electrochemistry.

Various carbon materials such as carbon fibers or carbon cloth can be used as support for the growth of nanotubes. As highly effective surface treatments, the localized etching by water vapor and the exposure to nitric acid vapor are used to enhance the number of surface defects. The iron catalyst for the nanotube growth was synthesized by wetting with iron nitrate, by chemical vapor deposition (CVD) of ferrocene, or by electrochemical iron deposition. Carbon nanotubes were subsequently grown on the iron-loaded fibers by pyrolysis of methane or cyclohexane. A highly dispersed, hierarchically structured catalyst support was obtained in this way.

Nitrogen-doped carbon materials have been used as metal-free electrocatalysts in the ORR. Some of the N-doped carbon catalysts show remarkable activities in the ORR especially under alkaline conditions, where the activities are often assigned to certain nitrogen groups and surface defects on the carbon surface. To elucidate the electrocatalytic mechanisms, a major challenge is the controlled synthesis of specific nitrogen groups on carbon surfaces.

Different methods were employed for the synthesis of nitrogen-doped carbon materials: (a) Catalytic growth of N-doped CNTs from N-containing organic precursors; (b) Post-treatment of oxygen-functionalized CNTs under ammonia atmosphere at elevated temperatures; (c) Post-treatment of oxygen-functionalized CNTs by pyrolyzing N-containing organic precursors at elevated temperatures; (d) Pyrolysis of N-containing polymers. The effect of these methods on the electrocatalytic properties will be discussed.

Fischer-Tropsch synthesis (FTS) is a well-established industrial process for converting synthesis gas derived from coal, natural gas or biomass over iron or cobalt catalysts into mainly linear hydrocarbons exhibiting a broad chain-length distribution. In particular, high synthesis temperatures and Fe-based catalysts are essential for short-chain α-olefins. Fe catalysts supported on active carbon were reported to have a higher activity per unit volume and higher olefin selectivity compared to unsupported catalysts. In my talk, I will report on Fe nanoparticles deposited on oxygen-functionalized CNTs (OCNTs) and on nitrogen-functionalized CNTs (NCNTs). Catalytic testing under industrially relevant conditions was applied to demonstrate the unique properties of OCNTs and NCNTs for the Fe-catalyzed high-temperature FTS. The obtained catalysts showed excellent olefin selectivities, moderate methanation tendency, low growth probabilities and good stabilities.

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PL-3

The Particle-Size Effect in Oxygen Reduction Electrochemistry on Platinum - from Model to Real Catalysts

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Fuel cells are considered as potential candidates for future energy conversion systems, low-temperature polymer electrolyte membrane fuel cells (PEMFC) are in particular interesting for mobile applications. The main fundamental problems of PEMFCs to date are a lacking practical efficiency, due to the high overpotential for the essential oxygen reduction reaction (ORR) and the degradation of the catalyst during operation. This typically results in the use of high amount of noble metal catalyst, which has to be avoided in order to reduce material and thus also system costs. An improvement for the overall catalytic activity of the ORR can be achieved by increasing the active surface area, i.e. decreasing the particle size. However, the gain for the most common catalyst Pt is less than expected, since the specific activity of the catalyst decreases for smaller particles. In this presentation the reason for the particle size effect will be discussed, and potential solutions for circumventing it will be addressed.

Features of Preparation of Carbon Supported Pt Catalysts for PEM Fuel Cells

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Devices providing direct conversion of chemical energy into electrical are referred to fuel cells (FC). The oxidant and/or fuel in the process flow out of an external source. The specified devices possess high efficiency, they are noiseless and when using hydrogen don't pollute environment.

Among the wide variety of FCs, proton exchange membrane fuel cells (PEMFC) including direct methanol fuel cells (DMFC) that convert the chemical energy of a fuel (hydrogen and methanol, respectively) and an oxidant (air or oxygen) into electricity occupy a special place. The chemical reactions occur in the presence of catalysts on the interface electrolyte - electrode. Carbon supported Pt-containing systems are the best known anode and cathode catalysts in PEMFC and DMFC. For these purposes, highly dispersed catalysts with an average size of metal particles less than 4 nm and with high platinum content up to 80 wt.% are claimed. The synthesis of such catalysts with a narrow size distribution of the supported particles represents a complex problem.

The main approaches, including those used at Boreskov Institute of Catalysis, to deliberate synthesis of anode and cathode electrocatalysts of PEMFCs effective in oxidation of hydrogen and lower alcohols are examined in the report. Some aspects related to development and research of Pt-containing catalysts for alkaline fuel cells using sodium borohydride as a fuel are considered. The report presents data on traditional methods of supporting an active component on carbon materials of the different nature based on adsorption and/or deposition of metal precursors with the subsequent their reduction on the carbon surface. The procedures including electrochemical deposition of Pt, a dispersion of colloidal metal particles and synthesis of catalytic systems with the structures of core-shell, hollow spheres and rattle type particles are also discussed. The analysis of characteristics of supported Pt-containing catalysts (composition, size, localization and the microstructure of surface particles) obtained by these methods and their efficiency as electrocatalysts for PEMFCs is made.

PL-5

Formation of Active States of the Hydrogenation Catalysts: from Oxyhydroxides to Metallic Nanoparticles

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Nanodispersed metallic particles of the 3d transition metals from Fe to Cu are widely used as hydrogenation and dehydrogenaton catalysts in many industrial processes, ranging from selective hydrogenation to hydrogenolysis and complete methanation. Hydrogenation activity and selectivity depends on the active metal: increasing d-factor strengthen hydrogenation ability for VIIIb group metals, while copper-containing catalysts are useful for more delicate impact on substrate. However the nature of the active metal isn't the sole factor which determines the performance of hydrogenation catalyst: many of hydrogenation processes were proved being structure-sensitive, therefore dispersion of the metallic particles affects its selectivity and activity; also surface defects, stacking faults and microstrain of crystal structure have significant effect on the catalytic properties. Strength of the interaction of metallic nanoparticles with the supporting oxide phase is one of the key parameters which regulate its size, shape, surface composition and structure. Examples of strong metal-support interaction (SMSI) phenomena are numerous, starting from pioneering works on Ni/titania system. "Wetting" of metallic surface with oxide phase alters the surface composition of metallic nanoparticle, it eases reduction of the cations of the support, as well as it causes oxidation of the active metal. In some cases wetting makes epitaxy between two phases thermodinamically favourable despite of the significant strain of metallic phase structure.

The extent of interaction between active metal and support is greatly dependent on chemical nature and structural parameters of the both components. Chemical composition and the structure of the precursor compound also affect the process of transition metal reduction, which leads to the active state. Therefore, the entire history of a catalyst starting from the precursor source and the way of the catalyst preparation has significance for the resulting catalyst performance. Studying kinetics of the catalyst reduction together with monitoring the structure of the catalyst can give insight of the evolution of the catalyst from oxyhydroxide precursor to the supported nanoparticles and allow understanding of reproducible production of the catalyst with desired performance.

A lot of attention is traditionally paid to cationic composition of the precursors, while the effect of the anionic promotion was not so widely discussed in literature. Recent studies of Cu-containing catalysts evolution showed that the presence of hydroxyl and carbonate anions may have dramatic effect on the kinetics of copper reduction from the mixed oxides, manifold changing the reduction activation energy (e.g. from 20 to 65 kJ/mol for Cu-Mg mixed oxide and from 110 to 40-45 kJ/mol for Cu-Zn mixed oxide catalyst). These effects may be ascribed to the changes of the local neighborhood of copper cations, which are induced by hydroxyl and carbonate admixtures. Also, the presence of nitrates in Co-Al hydroxycarbonate precursors affects the state of cobalt in the mixed oxide after the thermal treatment and changes not only the reduction process but the structure of active metal as well and improves the performance of the catalyst. Changing the gas flow composition (i.e. adding nictric oxide) at thermal treatment of precursor has similar effect.

Thus, the resulting performance of the catalyst can be improved at early stages of the catalyst preparation and treatment. This can be done by adjusting (1) the composition and the structure of the oxyhydroxide precursor; (2) the temperature of thermal treatment of precursor and composition of the gas flow at this stage; as well as by (3) choosing the optimal conditions of reductive activation of the catalyst. The fundamental studies on the peculiarities of each these stages contribute to the development of the hydrogenation catalyst with desired performance.

PL-6

Catalytic Transformations of Light Alkanes: Energy and Chemistry-Related Applications. Numbers and Values

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Fossil hydrocarbons (FHC) originated from oil and natural gas constitute a basis of the modern petrochemical and organic synthesis industries. They also remain the main source of energy for industry and transport, despite persistent attempts to involve other sources to chemical and energy production. Hence, the hydrocarbon market balance has a very strong impact upon the overall stability of the world economy. Consequently, the energy efficiency of hydrocarbon processing is one of the major factors determining the sustainable functioning of corresponding industries.

Light alkanes (LA) are the main components of natural and petroleum gases (which constitute about a half of the whole FHC production), as well as biogas. As LA are the most chemically stable organic compounds, catalytic transformations play the major role in their chemical processing for both chemical and petrochemical synthesis and for several applications in power engineering.

This presentation is mainly focused on the selective oxidative transformations of LA into value-added products (VAP) and for energetic applications. Such processes can be most efficiently carried out over oxide catalysts. Possible ways of LA molecule activation over oxides and the nature of catalyst active sites, as well as the nature and consecutive transformations of intermediates will be discussed. Since in the production of VAP selectivity is the main issue, mechanistic and kinetic aspects of selectivity in LA partial oxidation and related processes will be examined. The consideration of LA oxidation on molecular level will be followed by the analysis of the process in the enlarged reactor with heat and mass transfer complications.

Finally, some technical solutions which allow one to improve the overall chemical and energetic efficiency and, correspondingly, to optimize the utilization of FHC potential will be demonstrated and discussed.

KEYNOTE LECTURE

KL-1

Catalysis by Heterometallic Clusters Formed on Support Surface. Synergism and Structural Organization of Active Components

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In this communication analytical review of world-wide achievements, including the results of author's group, related to heterogeneous catalytic- and electro-catalytic reactions on Pt, Au, Ni, Pd, Zn mono- and hetero-metallic nanosized active components distributed on surface of Al_2O_3, ZSM-5 and TiO_2 supports will be presented. Special attention will be done on the evolution of catalytically active components during preparation and preliminary activation stages of catalysts, as well as on correlations between structure of metal-containing sites and their catalytic properties in reactions of natural gas and row of biomass products, such as methane, alcohols and rapeseed oil conversion into hydrocarbon fuel components, olefins, as well as the process of methane steam reforming for hydrogen producing. Using X-Ray, XAS, TEM, and Mössbauer spectroscopy it was shown, that non-additive increasing of activity and selectivity of materials can be provided by the forming of the clusters of metal-containing active components consisting of intermetallic, or core-shell configuration, or independent metal-oxide systems, undergoing with each other. Mechanistic aspects of reactions carried out will be considered.

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ORAL PRESENTATIONS

OP-1 ÷ OP-18
OS-1 ÷ OS-14

Investigation of Pt Electrode Surface Species during Gas-Phase Water Electrolysis by NAP-XPS

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The current energy debate has induced a lot of activities in the field of water electrolysis as a means of generating hydrogen as energy carrier. Research in material science is challenged to develop High efficiency electro-catalyst for the oxygen evolution reaction (OER) [1,2]. Deep understanding of mechanistic aspects of both the OER and the catalyst degradation upon OER are needed to enable nanoscale control of the catalytic properties for achieving high performance and long-term stability. In this work, the surface chemistry of a Pt/NAFION-based electrode is characterized in-situ during gas-phase water electrolysis by means of the near ambient-pressure X-ray photoelectron spectroscopy (NAP-XPS) end-station at the ISISS beamline (HZB/BESSY II).

Electrochemical techniques such as cyclic voltammetry (CV) and chrono-amperometry (CA) under relevant polarization are combined with simultaneous NAP-XPS investigation of the O1s, C1s, and Pt4f core levels and the gas composition is continuously monitored by mass spectrometry (on-line MS). The chemical state of Pt under in-situ OER will be discussed with respect to the Pt4f XP spectrum of a Pt foil anodically oxidized in acidic media. The results show that the Pt electrode is oxidised during of the OER reaction, but an intermediate state seems to play an important role in the reaction. This in-situ investigation allows individuating strategies for improving the long-term stability of Pt-based electrodes.

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OP-2

On Thermal Stability of Catalytic Membrane Reactors for Partial Oxidation of Methane

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Partial oxidation of methane (POM) and other light alkanes to syngas with the using of ion conducting oxygen semi-permeable membranes is currently considered as one of the most promising methods for primary processing of natural gas. Still, there are a number of significant impediments that prevent introduction of this technology into industry. Mostly they are concerned with insufficiently high oxygen permeability and thermodynamic stability, and exceedingly large thermal and chemical expansion. Fortunately, numerous research works in recent years have resulted in identification of promising materials that show good performance when tested as oxygen membranes for POM. For instance, high values for conversion (>99%) and selectivity (>90%) have been achieved in long term tests (7300 h) of tubular POM reactors with $La_{0.5}Sr_{0.5}FeO_{3-\delta}$ (LSF) membranes [1]. Another serious problem concerns with the optimal thermal regime of the process. Therefore, this study was aimed at examination of the heat balance in the POM reactor at different temperatures, selectivity and inlet gas composition.

The tubular ceramic LSF membranes were fabricated by extrusion. The density of the sintered membranes was about 95% of theoretical. The wall thickness, diameter and length were near 1, 10, and 30 mm, respectively. The commercial alumina was used as catalytic support in the form of small cylinders with the diameter of about 2 mm and 6–10 mm length. The support was soaked in solution of nickel nitrate, dried and fired at 1000°C for 5 hours in order to obtain the catalyst with 15% load of nickel. The catalyst was placed at the outer wall of the membrane in the stream of the feed gas. The stream of air was passed inside the membrane. The thermocouple for temperature control was placed at the inside wall of the membrane in the air stream. The outlet gas composition was analyzed with the help of a gas chromatograph.

Generally, the temperature increase of the membrane must result in respective increase of oxygen ion-electron conductivity and heat release, which evolves in the reaction of the feed methane with the oxygen permeate. The evolved heat, in turn, provides further increase of the membrane temperature. The calculations show that this process tends to be self-accelerating at sufficiently high-selectivity, and it may eventually result in breakdown of the membrane. In order to verify the calculated results the steady state of the POM process was achieved with the membrane temperature 850° C and selectivity for CO near 92%. Then, the temperature of the auxiliary external heater was gradually raised. It was observed that a moderate increase of the heater temperature resulted in about triple larger increase of the membrane temperature. Respectively, the oxygen flux increased at 1.5 times while selectivity decreased to near 70%. Additional experiments demonstrated that this unfavorable effect can be partially mitigated by the using of humidified methane. It is because endothermic steam reforming reaction consumes large amount of heat and, thus, helps to decrease the overheating of the membrane.

We have shown that the inherent thermal instability of the oxygen membrane in the partial oxidation of methane is most pronounced at high selectivity. This can lead to thermal imbalance of the reactor and to the loss of control over the process. In order to ensure good handling of the POM reaction special care should be taken concerning reactor design, composition of the feed gas and catalyst arrangement.

This work was partially funded by the Ministry of Education and Science of the Russian Federation (grant № 8649). Authors are also grateful to the Ural Branch of RAS for support of this study through the regional program Arctic (grant 12-3-2-002).

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OP-3

Oxygen Reduction: “À la recherche du catalyseur perdu”

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Fuel cell technology faces a major problem: oxygen reduction is slow and requires a sizable overpotential, which reduces the efficiency of energy conversion. This is particularly true of the most common type of low-temperature cell, the PEM (proton exchange membrane) cell, which is designed for applications in automobiles and portable devices. The PEM works only in acid solutions, where platinum is still the best catalyst, and therefore there is presently an intensive search for better and cheaper oxygen catalysts in this medium. Much theoretical work into the reaction mechanism and the electronic properties of catalysts, but all restricted to acid media, has paralleled this experimental activity. Oxygen reaction is faster in alkaline solutions, and comparatively cheap materials are better than platinum. What is missing for alkaline cells is a good, OH-conducting membrane, which would play the same role that PEMs play in acid cells. There are several, very promising approaches to the design of such membranes, and they may soon be commercially available. In any case, there are good reasons to investigate oxygen reduction in alkaline media theoretically.

On most electrode materials the first electron transfer to the oxygen molecule determines the overall rate. In strongly alkaline media this step is:

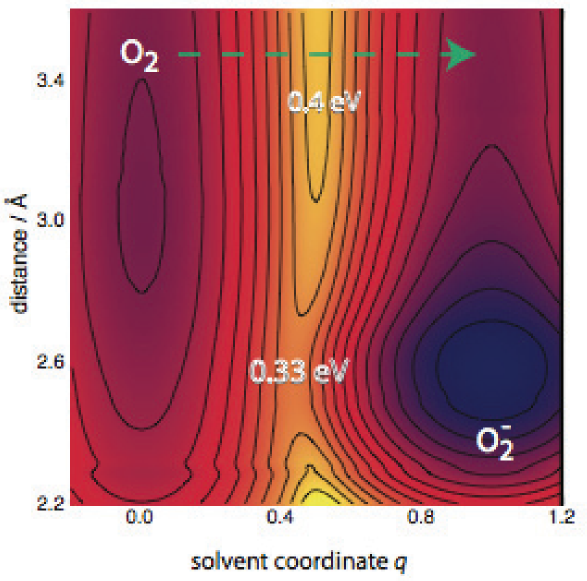
$$O_2 + e^- \rightarrow O_2^-$$

At low pH the first step is a combined electron and proton transfer:

$$O_2 + H^+ + e^- \rightarrow HO_2$$

In order to clarify the mechanism we have investigated the electron transfer to the oxygen molecule by our own theory. We combine the Density Functional Theory (DFT) results with our theory to calculate free energy surfaces for the reaction. As our model electrode we chose Au(100), which in alkaline solutions is one of the best catalysts. We first calculated the energy of the O_2 molecule in the vacuum as a function of the distance from the surface, optimizing the orientation and position parallel to the surface at each point. We also investigated the breaking of the oxygen bond trying various pathways. The lowest activation energy we found was about 2.2 eV. Obviously, bond breaking cannot be the first reaction step on Au(100).

The relevant properties of the solvent are known, and we can calculate the free energy surface of the reaction, which we shall plot as a function of the distance from the surface and of the solvent coordinate q. The latter indicates the configuration of the solvent, which during the electron transfer reaction changes from that appropriate to the molecule to that corresponding to the ion, the activated complex being somewhere in between. The following Figure shows the free energy surface calculated from our theory [1]:



At large distances there are two minima, one centered at q = 0, which corresponds to the oxygen molecule, and another one at q = 1 for the ion, and both have the same energy. The green dotted arrow between these minima indicates the outer sphere pathway (activation energy of about 0.4 eV). However, the favourable reaction path is clearly not outer sphere, but towards the deep minimum for the ion that appears at short distances and q = 1, and has an activation energy of about 0.33 eV. Au(100) is an excellent catalyst even though its interaction with the oxygen molecule is weak. All those effect, which control catalysis in acid media – position of the d band, long-range electronic interactions, adsorption energies of intermediates – seem to play no role. So what makes a good catalyst for oxygen reduction in alkaline media? According to our model it is the rate of the reactions after the transfer of the first electron.

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OP-4

Porous Ceramic Membrane-Catalytic Hydrogen-Containing Gas Generators for Compact Power Plants

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Porous ceramic membrane-catalytic systems (MCS) high-active in dry, steam and dry-steam conversion of light hydrocarbons (C_1-C_5), biomass conversion products (such as methane, ethanol, glycerol, acetic acid, as well as liquid crude fermentation products), exhaust products of Fischer-Tropsch synthesis and products of partial oxidation of aviation kerosene into syngas have been developed [1].

MCS are thermo resistant (>1000°C) porous ($\varphi \approx 40$ %, $d_{pore} = 1$-3 μm) ceramic membrane carriers of finger configuration, 17 mm length, 5.5 mm ext. diameter. MCS prepared by self-propagating high-temperature synthesis (SHS) using different mixtures of metal powders (Ni, Co, Al) and modified by sol-gel method using nanosized catalytic components on the basis of mono- and bi-metallic precursors of transition metals (La, Ce, Pd, Co, Mn, Zn). A buffer layer of TiO_2 has been formed in internal pore volume to increase a specific surface of membrane material [2].

Using optimal sample of MCS in steam methane conversion process at 800°C and flow rate about 37000 h^{-1}, 40 % of methane conversion was achieved, syngas composition $H_2/CO = 13.7$, syngas productivity ~9.6 $l/h \cdot cm^2$ (membrane reactor specific productivity is up to 60000 $l/h \cdot dm^3$).

A laboratory mock-up of a compact power plant (P is up to 100 W) where a module of MCS is integrated with a solid oxide fuel-cell was developed. Such system in operation mode produces electric current at a constant power of 60 W (I = 10 A, U = 6 V) using specified organic raw. Approximate estimation of non-optimized set-up efficiency in stable conditions at 800-850°C is ~ 70 %.

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Electrocatalysts for Oxygen Evolution Reaction: Behavior of Noble and Non-Noble Metal Oxides under Conditions of Oxygen Evolution

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Electrochemical water splitting with its ability to generate H_2 from a non-carbon based source can not only be used to store unused electrical energy at point of creation by converting it into chemical energy but is also likely to play a central role in the emerging carbon neutral economy [1,2]. Noble metal catalysts show near ideal behavior for the cathodic hydrogen evolution reaction. Challenges come from the anodic part in which oxygen is evolved. The anodic conditions are extremely oxidizing and this makes catalyst stability a serious issue under real operational conditions.

We at MPI CEC and FHI Berlin work towards developing a systematic understanding of the functioning of well known noble and non noble metal oxide (such as IrOx and MnOx) based catalysts. We are bringing together electrochemical techniques (voltammetry, amperometry and impedance spectroscopy) together with our traditional strengths in spectroscopy (X-ray, UV-VIS and Raman) and microscopy in systematically studying OER catalysts.

Our studies range from single crystalline surfaces to hydrous oxides. Our initial tests with Pt single crystalline electrodes show different OER activity for each surface in the order Pt(111) > Pt(100) > Pt(110) (Fig. 1). Electrochemical impedance spectroscopy in the OER potential regime shows a changing impedance spectra overtime which can be interpreted using a faradaic charge transfer model across a thin oxide film. The value interpreted as charge transfer resistance occurs in the inverse order of electrochemical activity. Metastable hydrous oxides are shown to form under high positive potentials (Fig. 2). We have further developed in-situ studies of metal oxide films based on UV and Raman spectroscopy with respect to studying IrOx and MnOx based oxides.

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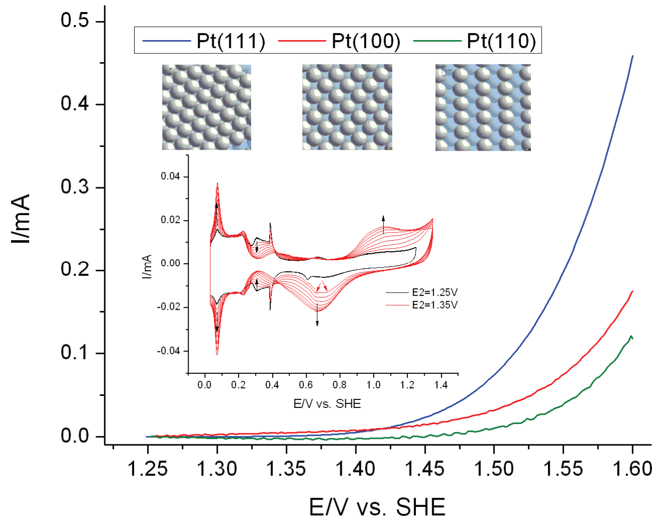

Fig. 1. Oxidation of Pt single crystalline surfaces.

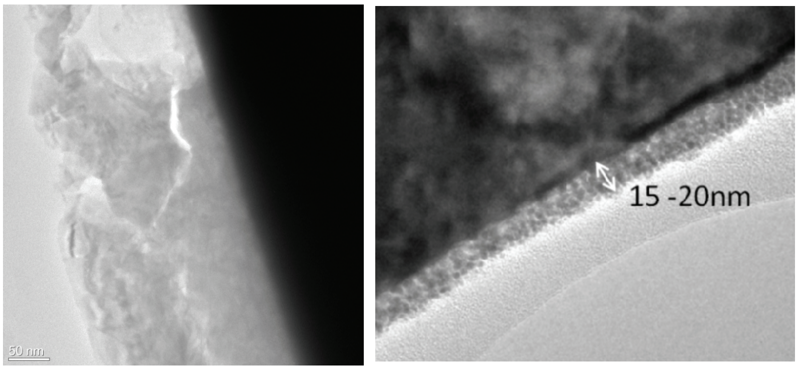

Fig. 2. TEM micrograph of anodized Pt foil. Pt forms thick and metastable oxo hydroxo layers when anodized at high potentials (left). Under open circuit conditions this metastable material decomposes (reduces) to form Pt nanoparticles (right).

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Supported Nickel Phosphide Catalysts for Methyl Palmitate Hydrodeoxygenation: Synthesis and Catalytic Properties

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Hydrodeoxygenation (HDO) are considered important commercial route for production of distillate range bio-fuels from triglyceride-based feedstocks such as vegetable oils, animal fats and non-edible greases, for example a tall oils [1]. Promising strategies of upgrading these bio-oils could be the direct hydroprocessing to produce hydrocarbons or the co-hydrotreatment with petroleum fractions, such as gas oil, to achieve the technical and environmental fuel standards. In recent years a considerable effort has been devoted to carry out a search of the catalysts which exhibit the high activity and stability in the presence of main hydrodeoxygenation by-products, such as CO and H_2O, and also aromatic, S-, N-containing compounds presented in petroleum feedstocks. The HDO selectivity of the catalyst (through the H_2O or CO/CO_2 removal) is a crucial factor for the process design and operation. The great interest as new alternative catalysts represent a supported nickel phosphides catalysts which has been demonstrated chemical and thermal stability, the higher activity in hydrodesulfurization [2], hydrodenitrogenation [3], hydrodeoxygenation [4] reactions than conventional sulfided catalysts. However, it was reported that the structure of nickel phosphide and catalyst preparation method have a significant effect in the activity and selectivity of the catalysts in hydrodesulfurization of dibenzothiophene [5] and hydrodeoxygenation of guaiacol [6].

The aim of the present work is to investigate the influence of various synthetic parameters on the formation of Ni_xP_y phase and on the catalytic activity and selectivity of silica-supported nickel phosphide catalysts in hydrodeoxygenation of methyl palmitate as the representative model components of triglyceride-based feedstock.

A series of silica-supported nickel phosphide catalysts were prepared by means of temperature-programmed reduction of the nickel phosphates or nickel phosphite precursors, with varying Ni/P molar ratios of 2/1, 1/1, and 1/2. The precursor of the Ni_xP_y/SiO_2 catalyst was reduced in a stream of H_2 (300 mL/min) at 450-650°C (heating rate 1°C/min) for 1 h and then cooled to room temperature. Finally, the sample was passivated in a flow of 1%O_2/He (30 mL/min) for 1 h at room temperature. The catalytic properties in HDO of the methyl palmitate (10 wt.%) was evaluated in trickle-bed down-flow reactor at the temperature 270-340^{o}C, hydrogen pressure 3.0-5.0 MPa, hydrogen/feed ratio 300-600, using *n*-dodecane as a solvent. The reaction products were identified by GC-MS and quantified by gas chromatography system equipped with DB-1 column and atomic emission detector (GC-AED). The total oxygen content in the reaction mixture was determined using CHNSO elemental analyzer Vario EL Cube. The catalysts were characterized by X-ray photoelectron spectroscopy, X-ray diffraction, and, transmission electron microscopy (TEM).

In HDO experiments the performances of Ni_xP_y/SiO_2 catalysts were compared in terms of conversion of methyl palmitate, oxygen removal, products yield, concentrations of normal alkanes in the liquid products. The effect of the different reaction conditions (temperature, hydrogen pressure, hydrogen/feed ratio, etc.) on the products distribution has been studied. It was shown that methyl palmitate completely transformed into saturated C_{15} and C_{16} hydrocarbons through the formation of monounsaturated C_{15} hydrocarbons and oxygen-containing intermediate compounds: palmitic acid and pentadecanal. The ratio of C_{16}/C_{15} hydrocarbons decreased in the products with increasing the temperature and decreasing the pressure, so the contribution of the decarboxylation/decarbonylation routes in the hydrodeoxygenation process increased. The synthetic parameters of Ni_xP_y/SiO_2 catalysts effects on the activity and selectivity of the methyl palmitate HDO routes by hydrodeoxygenation or decarboxylation/decarbonylation. The increase of the Ni/P molar ratio from 0.5 to 2.0 leads to increase of the average size of the nickel phosphide particles from 1.9 nm to 3.7 nm according to the TEM data, as a consequence the overall conversion of oxygen decreased in 2.6 times. The tentative reaction scheme of methyl palmitate transformation over Ni_xP_y/SiO_2 catalysts was considered.

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OP-7

Manganese Oxide Nanoparticles Supported on Carbon Materials for Electrocatalytic Water Splitting

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Electrocatalytic water splitting into hydrogen and oxygen realized with energy produced by solar photovoltaics, wind or hydro sources will play a major role in future technologies for regenerative energy storage. The hydrogen serves as energy carrier which can be used for combustion or with higher efficiency in hydrogen fuel cells to gain back the stored energy [1]. Therefore effective, durable and affordable materials are required.

Manganese oxide nanoparticles supported on carbon nanotubes (Fig. 1) seem to be a promising candidate as electrode material for electrocatalytic water splitting at neutral pH [2]. It was determined that the different preparation methods like symproportionation reaction and incipient wetness impregnation cause different electrocatalytic activities comparable to current MnO_x catalyst in strongly alkaline solutions [3].

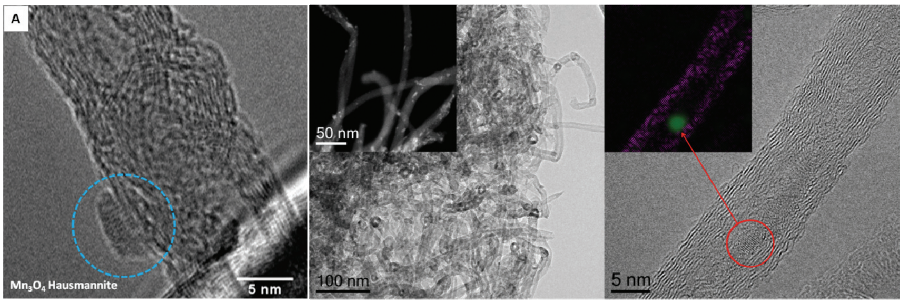

Fig. 1. TEM images of MnO_x particles supported on carbon nanotubes.

We investigated several carbon materials as supporting bases and the influence of preparation methods, MnO_x to carbon ratios and different calcination temperatures on the electrochemical properties. Further analytical characterization of particle sizes, shapes, distribution, thermal behavior and surface areas were performed by methods like TEM, SEM, XRD, N_2 physisorption, TG-MS and DSC.

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Methanol Decomposition and Oxidation on Pt and Pd

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Nowadays, availability and low cost of methanol stimulate permanent searches for new fields of its application. In particular, methanol is considered as the most promising alternative energy source. For instance, methanol can be used both in classical internal combustion engines and in direct methanol fuel cells for electricity production. It is also known that spark and diesel engines operated on fuel with addition of hydrogen or synthesis gas generate much lower level of harmful exhausts at even higher engine efficiency. The latest is of a special interest due to the possibility of hydrogen and synthesis gas production from methanol on board the car. Earlier, it was shown that both hydrogen and synthesis gas can be produced by the catalytic conversion of methanol on group VIII metals and Pt and Pd are more active in these reactions. To design better catalysts for on-board catalytic converters, a deeper understanding of the methanol surface chemistry on Pt and Pd is required.

The methanol decomposition and oxidation on Pt and Pd bulk catalysts were studied under ambient (0.01-0.1 mbar) pressures in the temperature range 300-650 K. We used temperature-programmed reaction spectroscopy (TPRS) to examine its catalytic performance depending on the molar methanol-to-oxygen ratio as well as near ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) to identify adsorbed reaction intermediates and to study the chemical state of catalysts under reaction conditions. The experiments were carried out using a VG ESCALAB HP electron spectrometer. The spectrometer was equipped with an X-ray source with a twin Al/Mg anode, a hemispherical electron energy analyzer, LEED optics, and a VG AG-2 ion source. The special high-pressure gas cell incorporated into the analyzer chamber of spectrometer, as well as the differential pump systems of the X-ray source and the electron energy analyzer, allowed us to measure *in situ* XPS spectra at pressures up to 0.1 mbar [1]. All spectra were acquired using the non-monochromatic Al$K\alpha$ radiation ($h\nu$ = 1486.6 eV) in the fixed pass energy mode. The experiments were performed using Pt(111) and Pd(111) single crystals with perfect (flat) and defect-rich surfaces. The using single crystals allowed us to compare not only selectivity but also activity of Pt and Pd because the methanol conversion value detected in the TPRS experiments can be easy converted to turnover frequency (TOF). Moreover, it also allowed us to study a role of defects in the methanol decomposition and oxidation. The “defect-rich” surfaces were prepared by

Ar^+-ions bombardment of the flat single-crystal surfaces for 10 min. For surface characterization LEED and scanning tunneling microscopy were used.

It was found that even in the oxygen presence the methanol decomposition on both Pt and Pd proceeds through two competitive pathways: fast dehydrogenation to CO and slow decomposition of methanol via the C-O bond scission. This conclusion bases on the observation of two features in the C*1s* spectra at 284 and 286 eV which correspond to carbon and CO adsorbed species. In contrast to ultrahigh vacuum conditions, in the mbar pressure range the rate of the second pathway is significant, which leads to a blocking of the catalyst surface by carbon and to a prevention of the further methanol conversion [1-3]. These carbon deposits are very active toward adsorbed oxygen species and, as a result, in the presence of oxygen fast methanol oxidation occurs at temperatures above 450 K [4]. CO, CO_2, H_2, and H_2O are detected as products in the gas phase. Increase in the oxygen content leads to increase in methanol conversion as well as in CO_2 and H_2O selectivities. For instance, a change in the O_2/MeOH molar ratio from 0 to 2 leads to an increase in methanol conversion rate (in TOF) on Pt(111) at 650 K from 0.3 to 18 s^{-1}; CO selectivity decreases from 100 to 6 %. It means that the main route of methanol reforming is the methanol dehydrogenation, while in the presence of oxygen, CO oxidizes to CO_2, and H_2 oxidizes to water. According to XPS, Pt and Pd are in the metallic state in all used conditions.

Using “perfect” and “defect-rich” single-crystal surfaces, we found that the methanol oxidation is a structure-sensitive reaction on Pt. So at 550 K, the methanol conversion rate on the defect-rich Pt(111) surface is a few times higher than on the perfect Pt(111) surface. Moreover, the CO selectivity at low oxygen content is also higher on the defect-rich Pt(111) surface. At 650 K, these effects fade out due to annealing defects. According to TPRS study Pd is more active in the methanol oxidation than Pt. The flat and defect-rich Pd(111) surfaces demonstrate similar catalytic performance. CO selectivity on Pd is comparable with that for the defect-rich Pt(111) surface at low oxygen content, while flat Pt(111) surface is more active in the total methanol oxidation.

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OP-9

Hydrothermal Synthesis of Carbon Materials from Polymer Precursors

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Carbon materials have attracted considerable attention due to their promising applications in catalysis, electrocatalysis, and hydrogen production [1]. In recent years hydrothermal carbonization (HTC) of renewable raw materials under very mild processing conditions (180°C) was developed. HTC is a more energy efficient method and low cost production method of carbon materials [2]. We focus on synthesis of carbon materials using polymer precursor such as polyvinyl alcohol or resorcinol by hydrothermal carbonization for further application as electrode in water splitting. These precursors have certain percentage of OH-functional groups that point to a carbonization mechanism driven by dehydration reactions. We investigated the influence of precursor and post-synthetic treatment of the samples at 650° C on the resulting carbon structure.

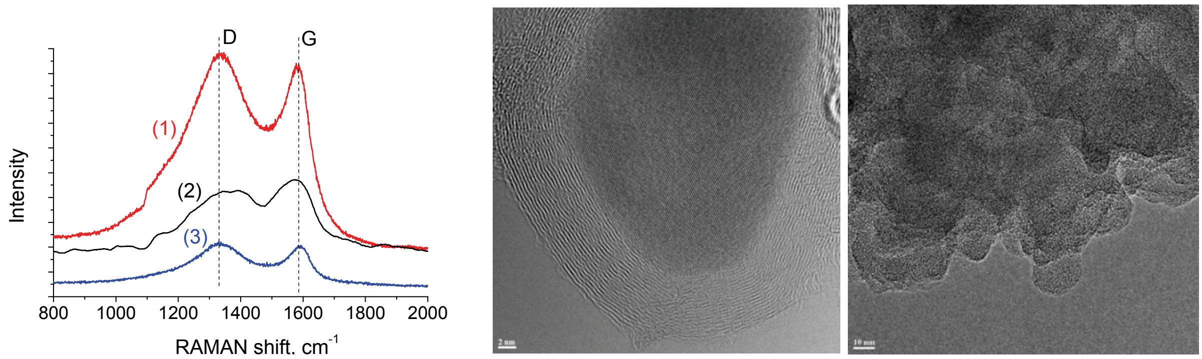
All samples were synthesized in autoclave system at a temperature of 220°C. We used different precursors: polyvinyl alcohol (PVA) or resorcinol for obtaining hydrothermal carbon materials. Iron ions were added to PVA solution since they act as graphitization catalyst. The samples were washed using different procedures with HNO_3 and HCl solutions [3]. We also carried out post-synthetic treatment. The materials were characterized by elemental analysis, TG-MS, XRD, IR, RAMAN, nitrogen adsorption and electron microscopy.

According to elemental analysis the samples prepared from pure PVA or resorcinol contain ~67-70 wt.% of carbon and ~25% of oxygen due to the presence of oxygen-containing groups in the sample (-OH, -C=O, -C-O). This fact is confirmed by IR, which indicates lines at $\nu_{OH} = 3420$, $\nu_{C=O} = 1710$, $\nu_{C-O} = 1072$ cm^{-1}. These samples do not show any graphitic domains; there are no D- and G-bands in RAMAN-spectrum. Post-synthetic treatment at mild temperatures should be carried out.

The elemental analysis of iron-containing samples indicates that washing with HNO_3 results in formation of iron oxides which is confirmed by elemental analysis (~30% wt.% Fe), IR spectroscopy (Fe-O line at 580 cm^{-1}) and XRD analysis. On the other hand, washing with HCl practically removes iron from the sample. In both cases the RAMAN spectroscopy indicates amorphous carbon which is determined by D- and G-bands.

Based on the results of TG-MS experiments, post-synthetic treatment of the samples was carried out at 650°C in Ar flow. After this treatment D- and G-bands appear in RAMAN-spectra of the samples synthesized from pure PVA or resorcinol that indicates formation of amorphous carbon. Post-synthetic treatment of the sample with high iron content promotes transformation from micro- to mesoporous structure. This sample is transformed to iron carbide that is confirmed by XRD and electron microscopy. TEM shows that we obtained Fe3C encapsulated graphitic carbon. Besides, in case of sample with 1 wt.% of iron amorphous carbon structure was revealed on TEM images.

Obtained results indicate influence of used precursors and post-treatment procedure on structure of HTC materials. It was shown that extended graphitic structure for the samples synthesized from pure PVA or resorcinol can be obtained only after heat treatment at 650°C. Addition of iron ions to solution of PVA results in formation of graphitic domains already at hydrothermal carbonization conditions. Excess of iron can be removed by washing samples with HCl.



(a) (b) (c)

Figure 1: a) RAMAN spetra of the samples synthesized from (1) PVA (HTC, 650°C), (2) PVA (1% Fe, HTC), (3) Resorcinol (HTC, 650°C); TEM of samples synthesized from (b) PVA (60% Fe, HTC, 650°C), PVA (30% Fe, HTC, 650°C).

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OP-10

Structural Dependence of Hydrothermal Carbon on Synthesis Parameters

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The diminishing fossil resources and the steady increase in energy demand require sustainable materials and process solutions for future energy supply. The efficient use of renewable energy resources, such as wind and solar energy, strongly depends on storage solutions which are able to buffer daily or seasonal fluctuations of power supply. One possible storage solution is the synthesis of energy-rich hydrogen or hydrogen-derived compounds, such as CH_3OH and NH_3 [1]. The most abundant hydrogen source is water. Thus, the electrocatalytic water splitting process can be considered as the most important process of chemical energy storage on a global scale.

As sustainable basis of electrode materials in the water splitting process, carbon from hydrothermal carbonization (HTC) can be applied. HTC can process renewable feedstocks, such as cellulose based biomass, under mild reaction conditions [2]. Since the hydrothermal synthesis provides a broad range of variable and controllable synthesis parameters, we investigate the influence of the process parameters on structural properties and electrocatalytic stability of the final product. All materials are synthesized in stainless steel autoclaves equipped with corrosion stable teflon liners. Typical synthesis temperatures range between 180-220°C, while the reaction pressure is about 10-25 bar according to the vapour pressure of water. We systematically varied the composition of the initial product solution, as well as the reaction temperature, the reaction time and the starting pH. The obtained HTC was tested by elemental analysis, TG-MS, IR, Raman, BET and electron microscopy.

We determined a significant dependency of structural properties of the HTC on the concentration of HNO_3 and thus the starting pH of the initial solution (Fig. 1). In particular, in the range of pH 0 to pH 3, the IR spectra show an inversion of the ν(C=O)- to ν(C=C)-ratio, while the carbon content, determined by elemental analysis, decreases only slightly from 68.8 % (pH 0) to 68.0 % (pH 3) (Fig. 1b). Macroscopic changes in morphology could be observed between pH 2 and 4. The colour of the powder samples changed from brown (pH 4 and higher) into black (below pH 2), while the bulk density increased by a factor of 4 for pH 2, in comparison to samples synthesized at pH 4 or higher (Fig. 1c).

All findings indicate a strong dependency of the degree of condensation of the HTC product on the initial pH. Since the final electrode materials require extended graphitic domains, in order to provide electron conductivity and stability in the electrocatalytic process, the use of low starting pH is advantageous. However, in applying a low starting pH in the synthesis is accompanied by high oxidizing strength of the solution which causes total oxidation of the carbon and CO_2 formation. The latter is indicated by pressure increases observed for the synthesis at low pH and the decreasing carbon yields for pH < 4. The use of non-oxidizing acids, such as HCl, however, was found to be inefficient in HTC synthesis. Consequently, an optimal balance of oxidizing strength, as well as H^+ concentration is required in the synthesis process. The results obtained in this work build the basis of further studies on mechanistic understanding of the polycondensation processes in HTC synthesis.

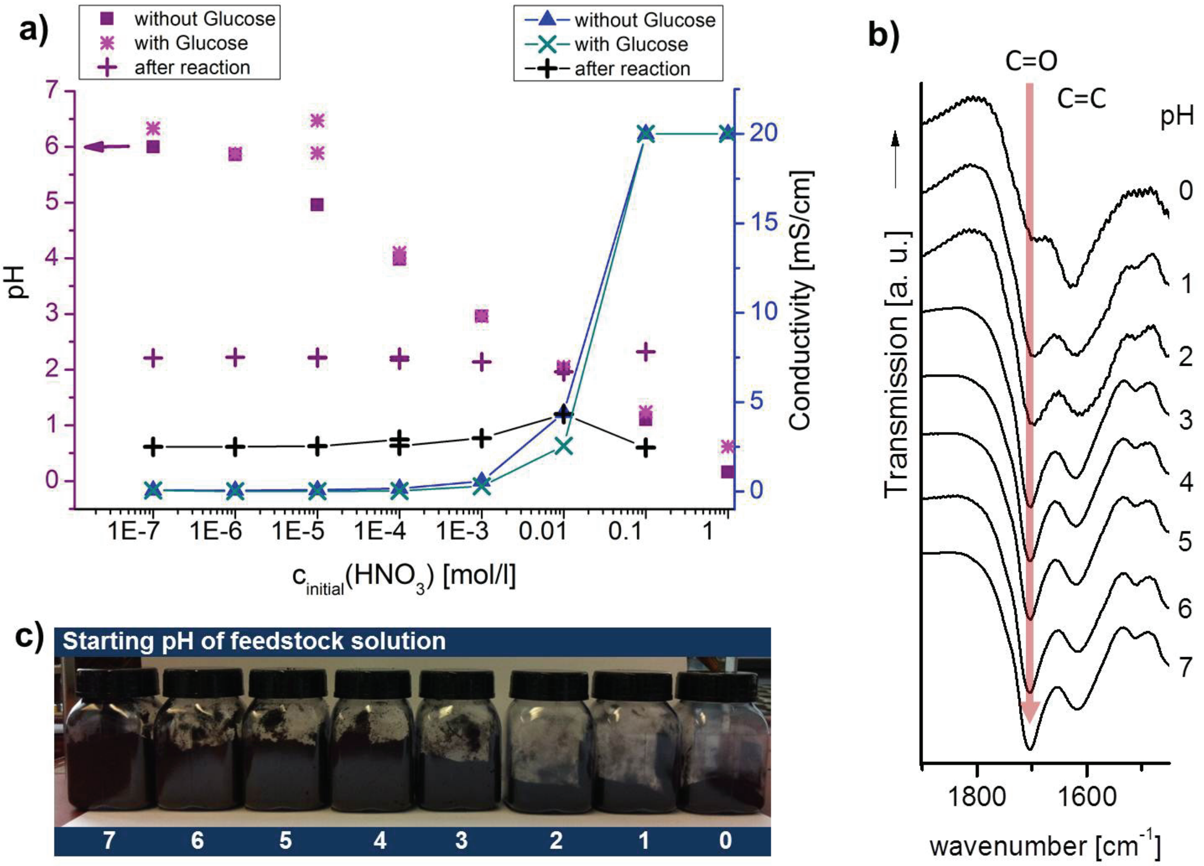

Figure 2: a) Dependency of pH, conductivity and HNO_3-concentration of initial product solutions; b) Comparison of IR-spectra of final product: Evolution of ν(C=O)-vibration of HTC prepared at increasing synthesis pH; c) HTC carbon obtained from 6 g glucose at different pH of initial solution.

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OP-11

Photocatalytic Hydrogen Production under Visible Light Irradiation from Aqueous Solutions of Organic and Inorganic Compounds

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Hydrogen as environmental friendly and high-energy fuel has attracted attention all over the world for the last decade. Photocatalytic water splitting under the visible light is a very promising and interesting method of the hydrogen production. However, because of the back reaction of H_2 and O_2 to give H_2O and the recombination of photoinduced electron and hole on semiconductor surface, the photocatalytic efficiency is usually low. In order to achieve higher efficiency for photocatalytic water splitting, many researchers in this field have involved electron donors as “sacrificial agents”, which can react irreversibly with the formed oxygen or photoinduced hole [1]. From a practical point of view, the electron-donating compounds should be cheap and easy to obtain. In this research we chose Na_2S/Na_2SO_3 system and ethanol as inorganic and organic electron donors for the H_2 production. H_2S occurs widely in natural gas fields and is produced in large quantities as an undesirable by-product in the coal and petroleum industry [2], ethanol is often used for the H_2 production because it is cheap and available product.

CdS was the first photocatalyst to be employed in H_2 production by irradiation of its aqueous solutions with visible light using sulfide ions as electron donors. Unfortunately, CdS is prone to produce photocorrosion in the reaction by the photogenerated holes. A possible way of enhancing the photocatalytic activity of cadmium sulfide is to develop composite materials based on CdS and the other sulfide semiconductors, for example, ZnS or CuS. The other way of the photocatalytic activity enhancement is a coupling of sulfide and oxide nanoparticles. This research aimed at the development of the semiconductor $CuS/Cd_{1-x}Zn_xS$ and $Cd_{1-x}Zn_xS/ZnO/Zn(OH)_2$ photocatalysts for the hydrogen production from Na_2S/Na_2SO_3 and ethanol water solutions under visible light.

The $Cd_{1-x}Zn_xS$ solid solutions were synthesized by two-step synthesis with $Cd(OH)_2$ and $Zn(OH)_2$ intermediates, proposed earlier [3]. The synthesis techniques of the photocatalysts were quite similar. For the $CuS/Cd_{1-x}Zn_xS$ photocatalysts preparation, a proper amount of $Cu(NO_3)_2$ was added in the stage of hydroxides formation; for the $Cd_{1-x}Zn_xS/ZnO/Zn(OH)_2$ photocatalyst in the lack of sodium sulfide was added in the stage of the conversion of hydroxides into sulfides. Photocatalytic H_2 evolution from ethanol and Na_2S/Na_2SO_3 water solutions was carried out by the following method. Water suspension with the catalyst and substrate was placed in a sealed reactor, purged with Ar and illuminated by a 1000 W high-pressure mercury lamp using a cutoff filter ($\lambda \geq 420$ nm).

Photocatalytic hydrogen evolution from Na_2S/Na_2SO_3 water solutions. Among the $Cd_{1-x}Zn_xS$ photocatalysts, $Cd_{0.3}Zn_{0.7}S$, which has a band gap of 2.71 eV, exhibited the highest activity. In order to improve the photocatalytic activity copper sulfide was added to $Cd_{0.3}Zn_{0.7}S$, the molar percent of Cu varied from 1 to 10. The highest activity was shown by the 1%$CuS/Cd_{0.3}Zn_{0.7}S$ photocatalyst. At optimal process parameters (pH = 9.7, C (Na_2S/Na_2SO_3) = 0.1/0.02M, C_{kat} = 0.77g/L), the rate was 1104 µmol/g*h and quantum was up to 23.5%, which is a large value for a process occurring under visible light on a catalyst containing no noble metal.

Photocatalytic hydrogen evolution from ethanol water solutions. Among the 1% $Pt/Cd_{1-x}Zn_xS$ photocatalysts, 1% $Pt/Cd_{0.2}Zn_{0.8}S$ exhibited the highest activity in the hydrogen evolution from water solutions of ethanol under visible light. The next step of our investigation was to compare the 1% $Pt/Cd_{0.2}Zn_{0.8}S$ photocatalyst with the 1% $Pt/Cd_{1-x}Zn_xS/ZnO/Zn(OH)_2$ multiphase photocatalysts. The hydrogen evolution rate in the case of using the multiphase specimen $Pt/Cd_{0.33}Zn_{0.67}S/ZnO/Zn(OH)_2$ was 2-fold higher than the rate observed for the photocatalyst $Pt/Cd_{0.2}Zn_{0.8}S$. Therefore, the multiphase photocatalysts is more effective in the H_2 production from ethanol water solutions under visible light likely due to the sulfides photocorrosion decrease.

In conclusion, prospective semiconductor photocatalysts for the photocatalytic hydrogen evolution from both oraganic (C_2H_5OH) and inorganic (Na_2S/Na_2SO_3) electron donors were proposed. It was shown that for the Na_2S/Na_2SO_3 system the 1%$CuS/Cd_{0.3}Zn_{0.7}S$ photocatalyst possesses the highest activity, whereas for the organic electron donors the multiphase 1% $Pt/Cd_{1-x}Zn_xS/ZnO/Zn(OH)_2$ is preferable.

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OP-12

One-Step Hydroconversion of Vegetable Oil to Premium Diesel Fuel Components on Pt/B_2O_3-Al_2O_3 Catalyst

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Declining petroleum resources combined with environmental concerns about fossil fuels determine the expediency for development of energy-efficient processes of fuels production from plant biomass. In this respect, hydrodeoxygenation (HDO) of vegetable oils is the promising process for obtaining green diesel fuels. Products of vegetable oil HDO are free of sulfur, nitrogen and aromatic compounds and consist mainly from n-alkanes C_{15}-C_{18}. Hovewer due to significant amounts of n-alkanes such fuels display higher cloud points and pour points thus limiting their applications. To improve the low-temperature properties of HDO products the additional stage of hydroisomerization is required. Thus, the development of bifunctional catalysts based on acidic carrier with supported metal [1-5] which provides one-step conversion of vegetable oil to diesel fuel is of high importance. In this work we optimize the conditions of vegetable oil hydrodeoxygenation process on Pt/B_2O_3-Al_2O_3 catalyst and evaluate the catalyst stability.

Acidic support B_2O_3-Al_2O_3 was obtained by adding of orthoboric acid to pseudoboehmite with following drying at 120°C and calcination at 550°C. Platinum (0.5 wt.%) was added by incipient wetness impregnation of the support with aqueous solution of H_2PtC_{l6}. The obtained material was then dried and calcined at 500°C. Catalytic experiments were carried out in a fixed bed flow reactor in the presence of hydrogen at 330-430°C, 1-4 MPa and weight hourly space velocities (WHSV) of 1-5 h^{-1} during 20 hours time on stream. Prior to experiment the catalyst was reduced at 500°C. Refined sunflower oil was used as a feed. The stability of the catalyst was evaluated by the testing at optimal conditions during 100 h.

Hydrodeoxygenation of vegetable oil on Pt/B_2O_3-Al_2O_3 catalyst proceeds with total oxygen elimination. The yield of liquid products in all studied conditions (excluding 330°C) is in the range of 71.1-77.6 wt%. The main hydrocarbon products at 350°C are n-alkanes C_{17}-C_{18} which are formed by decarboxylation, hydrodecarbonylation and hydrogenation/dehydration reactions. Due to suppression of the hydrogenation function at higher temperature (400°C) the intensification of decarboxylation reactions occurs leading to the formation of intermediate alkenes. These intermediate compounds undergo isomerization and cracking on acid sites with subsequent saturation on metal sites. As a result the product is enriched with isoalkanes. Thus, at WHSV of 0.5-1.0 h^{-1} and temperature of 400°C obtained diesel fraction (boiling range of 200-350°C) contains up to 55.5 wt.% of isoalkanes. At higher WHSV (5.0 h^{-1}) metal sites contribute to the formation of aromatic compounds probably due to lower hydrogenation rate in comparison with cyclization rate. Decrease of the process pressure from 4 to 1 MPa is accompanied by intensification of aromatization reactions leading to lower yield of the products of isomerization and hydrocracking. Thus, the following conditions of vegetable oil hydrodeoxygenation on $Pt/B_2O_3-Al_2O_3$ catalyst are considered as optimal: 400°C, 4 MPa and WHSV of 1.0 h^{-1}. In these conditions during 20 h time on stream the yield of diesel fraction is 72.5 wt.% with isoalkanes content of 55.5 wt.%. After 100 h time on stream diesel fraction yield increases to 84.6 wt.%. At the same time isoalkanes content in diesel fraction decreases to 37.4 wt.% probably due to blocking of acid sites of the catalyst by unsaturated compounds formed during hydrodeoxygenation process. Investigation of the spent $Pt/B_2O_3-Al_2O_3$ catalyst (after 100 h time on stream at 400°C) by IR spectroscopy and UV-Vis spectroscopy revealed the presence of unsaturated cyclic compounds on its surface.

It is shown that $Pt/B_2O_3-Al_2O_3$ catalyst provides complete oxygen elimination in one-step hydroconversion of vegetable oil at 400°C, 4 MPa and WHSV of 1.0 h^{-1} for 100 h time on stream. During the process isoalkanes concentration in diesel fraction decreases from 55.5 to 37.4 wt.%.

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OP-13

Mn/Sn Mixed Oxides for the Oxygen Evolution Reaction

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"Ekolyser" is a collaborative project financed by the German Ministry of Economy (Bundesministerium für Wirtschaft). It involves partners from the academic and industrial worlds (Jülich Research Center, Solvicore GmbH, FuMA-Tech GmbH, Max Planck Institute for Chemical Energy Conversion, Fritz-Haber Institute of the Max-Planck Society and Gräbener Maschinentechnik GmbH). The aim is the development of new cost-effective and sustainable materials for a commercially viable PEM-water electrolysis setup for hydrogen production from renewable energy sources. Energy storage is one of the key features of the industrial revolution implied by the shift towards renewable energies. Indeed the intermittent nature of renewable energy sources considerably inhibits their widespread use for the time being. Hydrogen produced by such means reversibly stores energy harvested from green energy sources and would allow for a complete remodeling of the power supply chain.

In order to prepare the broad commercialization of PEM-electrolyzers after 2015, priority is given to the cost-reduction of the production of such systems. We are focusing mainly on the reduction of the noble metal loading in the catalytic materials covering the anode, where the Oxygen Evolution Reaction (OER) takes place and where the biggest potential for improvement is expected [1]. The goal is to achieve a reduction of 90% of the Pt-group metal loading (i.e. a resulting loading of 0.6 mg $Ir.cm^{-2}$ and 0.2 mg $Pt.cm^{-2}$) while maintaining the performance and long-term stability of the electrodes. As an earth-abundant alternative, MnO_x-based catalysts are very recently attracting a lot of attention: Gorlin et al. have extensively studied the electrocatalytic activity of nanostructured Mn(III)-oxide electro-deposited as thin films on glassy carbon substrates [2]. They claimed high bifunctional activity for the Mn(III)-based catalyst in OER as well as ORR (Oxygen Reduction Reaction), comparable to the activity of the best precious metal catalysts. In order to improve the corrosion resistance of such catalysts over long periods of use, Sn has been proposed as a corrosion inhibitor [3].

Hence, our primary goal is the production of mixed Mn/Sn oxide precursors by easily scalable solvo-thermal synthesis methods. We have produced $Mn^{II}Sn(OH)_6$-type materials by a constant pH polycondensation method, as well as $Mn^{IV}O_2/SnO_2$-type materials using the synproportionation of Mn(II) and Mn(VII) in controlled conditions. A central requirement for electrode applications is to achieve high conductivity of the electrocatalytic material. Carbon material is often added for this purpose. However deactivation of the electrocatalysts through coking is often the result. Hence a central objective of our work is to improve the conductivity of our samples through thermal treatment in various gas atmospheres. The samples are first treated in oxygen-rich atmospheres, in order to tune the oxidation state of Mn. Indeed, Mn^{III} and M^{IV} are both believed to play a central role in the OER reaction [4]. Further treatment in mildly reductive atmospheres (H_2, MeOH) aims at improving the conductivity of the bulk material. Eventually the electrocatalysts are tested for their catalytic activity as anodic material for the OER-reaction, both in an electrolyzer setup coupled to mass spectrometry for analysis of the evolved gas phase, as well as in a sacrificial agent experiment using Ce^{IV} as a first screening method of the intrinsic catalytic activity [5].

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OP-14

Hydrogen Production by Steam Reforming of Dimethoxymethane

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Proton exchange membrane fuel cell (PEM FC) and high temperature proton exchange membrane fuel cell (HT PEM FC) are considered as an alternative environmentally sound source of electric power. These fuel cells are usually fed by pure hydrogen or hydrogen-rich gas mixtures produced by catalytic conversion of hydrocarbons or oxygenated hydrocarbons. Dimethoxymethane (DMM) also called methylal is a synthetic oxygenated organic compound as it can be produced by either condensation reaction of formaldehyde with methanol, or direct catalytic oxidation of methanol. DMM – a green material with extremely low toxicity – finds numerous applications [1].

It has been found recently [2] that DMM can be easily steam reformed to hydrogen-rich gas at relatively low temperature (250-350^{o}C) on complex (mechanically mixed) catalysts consisted of active solid acid and copper-based systems.

Overall DMM steam reforming (SR) is expressed by equation:

$$CH_3OCH_2OCH_3 + 4H_2O = 8H_2 + 3CO_2 \qquad (1)$$

Besides, during this reaction, a reverse WGS reaction may proceed to produce carbon monoxide:

$$CO_2 + H_2 = CO + H_2O \qquad (2)$$

It is generally assumed that DMM SR (eq.1) proceeds via consecutive reaction mechanism:

$$CH_3OCH_2OCH_3 + 4H_2O = 2CH_3OH + CH_2O \qquad (3)$$

$$CH_3OH + H_2O = CO_2 + 3H_2 \qquad (4)$$

$$CH_2O + H_2O = CO_2 + 2H_2 \qquad (5)$$

The first step (eq.3) is hydration of DMM into methanol/formaldehyde over solid acid catalyst and the second step (eqs.4, 5) is methanol/formaldehyde SR to hydrogen-rich gas over steam reforming Cu-based catalyst. Therefore, the active and selective DMM SR catalyst for the production of hydrogen-rich gas must contain the sites of dual functionality, provided by the acid and steam reforming species.

This presentation reports our recent results on the development of catalysts for DMM SR to hydrogen-rich gas. We demonstrate that:

- mechanical mixture of solid acids (γ-Al_2O_3) and copper containing catalysts (CuO/CeO_2), as well as bifunctional (CuO-CeO_2/γ-Al_2O_3, CuO-ZnO/γ-Al_2O_3) catalysts containing on their surface both acidic and copper-based sites, are active and selective for DME SR to hydrogen-rich gas with low CO content. In particular, some of the developed catalysts provide a 100% conversion of DMM and hydrogen production rate of ca.600 mmol $H_2/(g_{cat} \cdot h)$ at 250-350° C;
- DMM SR to produce hydrogen-rich gas for PEM FC and HT PEM FC feeding applications seems to be promising alternative to methanol and dimethyl ether steam reforming.

Acknowledgements

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Oxidative Dehydrogenation of Light Alkanes over Vanadium-Magnesium Nanocrystalline Oxides

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Light olefins are important chemicals in synthesis processes because of their high chemical activity in certain reactions. Propylene, one of the most valuable petrochemicals, is nowadays produced either by steam cracking of liquid feedstocks or is recovered from off-gases produced in fluid catalytic cracking units in refineries. The remainder of propylene is produced via on-purpose technologies such as propane dehydrogenation and metathesis [1]. These processes suffer from thermodynamic limitations, coke formation and require costly heat exchange at high operating temperatures. As a result of these substantial drawbacks, the petroleum industry has sought a solution to the demand for olefinic hydrocarbons in the use of oxidative dehydrogenation (ODH) methods. ODH uses oxygen to react with the hydrogen released from the hydrocarbon, in situ, so that the aforementioned equilibrium limitation is removed, and high single pass yields can be achieved. The reaction is exothermic overall and does not require a supply of heat as in endothermic dehydrogenation reactions.

Among the diversity of catalytic systems developed for oxidative dehydrogenation reaction the aerogel-prepared nanocrystalline catalysts are considered to be one of the most promising ones. Aerogels are the materials to be synthesized by drying of gels in supercritical conditions i.e. in the absence of the superficial tension which allows one to avoid the collapse of pore structure. Use of this technology results in obtaining the materials with the small particles size, very high surface area, along with considerable quantity of superficial defects and low density that makes them very promising for application as adsorbents and catalysts. It is well known that the physicochemical properties of very small oxide crystals essentially depend on their size. Various nanocrystalline oxides synthesized via aerogel technique have been widely investigated in various catalytic processes [2].

Magnesium oxide is known to be one of the most interesting oxide systems for which the nanosize effects are the most significantly expressed. As it was elucidated in our earlier studies, the unit size of MgO particle plays a defining role for its apparent activity and reaction ability. The addition of vanadium results in a switch of activity to produce propene with appreciable selectivity.

In our work the series of the nanocrystalline VO_X/MgO catalysts has been synthesized using the aerogel technique. At the first stage joint aerogel hydroxide $VMg(OH)_X$ has been obtained after drying in autoclave in supercritical conditions. The synthesized $VMg(OH)_X$ samples were characterized by turbostratic layered structure (XRD data) and very high surface area (~ 1200 m^2/g). Then, nanocrystalline VO_X/MgO oxides were prepared by means of "delicate" dehydration of corresponding hydroxides in specially developed programmed temperature mode. As shown on Fig.1, the synthesized aerogel VO_X/MgO oxide system is represented by assemblies of cubic crystallites of about 5 nm in average size. The proposed aerogel technique allowed us to achieve the quite uniform distribution of vanadium in MgO structure within the wide range of loadings (1-26 wt.% by V_2O_5).

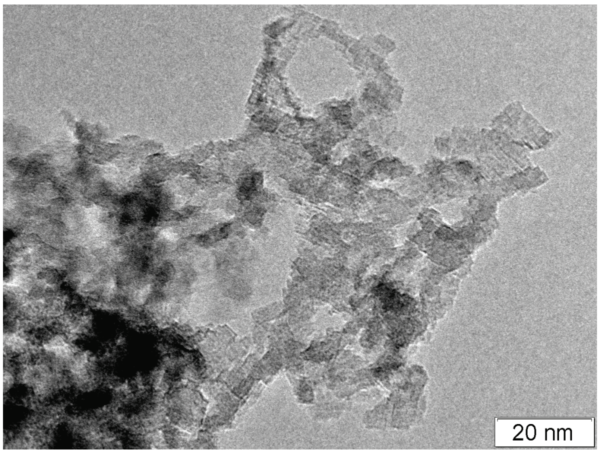

Fig.1. Microscopic image of aerogel-prepared 10%VO_X/MgO catalyst; TEM data.

The catalytic performance of nanocrystalline aerogel VO_X/MgO catalysts in ODH of propane and ethane has been compared with similar reference samples prepared via conventional methods (impregnation of aerogel-prepared MgO and mechanical mixing). According to catalytic testing results, the aerogel VO_X/MgO oxides with highly dispersed vanadia species tuned to be more active and more selective towards olefin production.

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OP-16

Ni-Based Catalysts in Dry Reforming of Methane – Study of Coking Behaviour

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During the past decades the emission of the greenhouse gas CO_2 by the fossil power plants has been significantly raised [1]. Among the major greengages CO_2 contributes 9-26% of the greenhouse effect. The contributions of water vapor and of CH_4 are 37-70% and 4-9% correspondingly [2]. Thus, the development of efficient utilization of these molecules into useful chemicals and fuels is a fundamental issue for a prospective, resource-saving energy management. To the present time the conversion of H_2O, CO_2 and CH_4 is based on the reforming technologies which aim to produce syngas CO/H_2 and is used as a significant technological step in the production of methanol, ammonia and high quality gasoline. Many reforming technologies have been introduced in response to the increasing demand of syngas, including dry (carbon dioxide) reforming of methane (DRM: $CO_2 + CH_4 \rightleftarrows 2CO + 2H_2$), the more traditional steam reforming of methane (SRM: $CH_4 + H_2O \rightleftarrows CO + 3H_2$), and partial oxidation of methane (PTM: $CH_4 + O_2 \rightleftarrows 2CO + 2H_2$).

Depending on the natural gas quality and required CO/H_2 ratio of the syngas a combination of this processes is used. However there are performed investment calculations showing that the DRM has an essential cost advantage over SMR. In the DRM, a highly endothermic reaction, noble metal-based catalysts are very active and stable. Active base-metals, in particular Ni-based catalysts have a low cost und wide availability but are more prone to fast deactivation by coking, oxidation and poisoning. The carbon deposition originates mainly from the exothermic methane and CO decomposition reactions and causes damage of reformers. For the catalyst development the primary challenge is the preparation of a noble metal-free catalyst that is kinetically more resistant against coking and thermally stable against sintering at elevated temperatures. It has been reported, that the addition of basic metal oxides such as MgO can deplete the carbon formation [4]. Herein, we present an investigation of the coking behavior of Ni bulk catalysts derived from hydrotalcite-like (htl) precursors. We report the effect of varied MgO and Ni contents on catalytic activity, microstructure and coke formation studied by means of TEM, Raman, TGA and catalytic measurements.

Phase-pure and crystalline NiO/MgAlO$_x$ precursors have been prepared using a constant pH co-precipitation method at 50°C with $0 \leq x \leq 0.5$ (Ni loadings ranging from 0 to 50 mol% in the final catalyst) at pH 8.5 and subsequent calcination (600°C, air). In our contribution we will elaborate structure-activity-coking correlations of the prepared Ni catalysts. The ex-htl catalysts (50 mol% Ni) show high activities and outstanding stabilities in DRM at 900°C (Fig. 1a.) but considerable deactivation at 800°C during 10 hrs. The loss of the activity correlates with the results of a thermogravimetric study, where rapid carbon formation with 9 wt.%/hr was observed at 800°C (Fig. 1b). An analogous experiment at 900°C showed that the catalyst might undergo less coking under operating conditions in a real catalytic reactor.

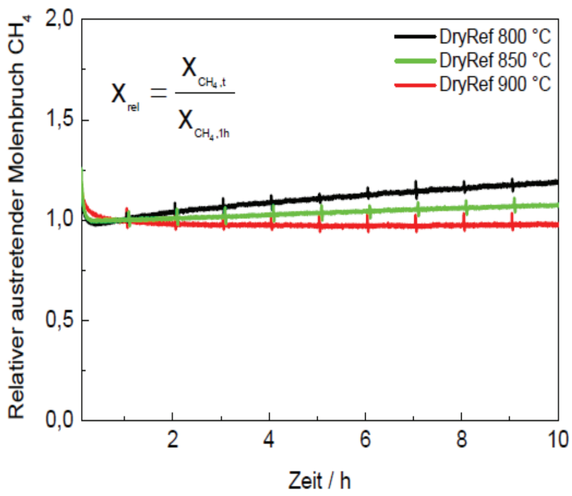

Fig. 1a. Comparative 10 h DRM tests at 800 and 900°C of Ni50-red800 → higher stability at 900°C

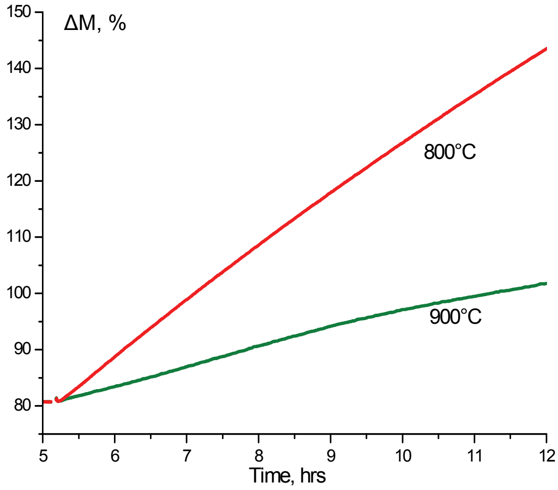

Fig. 1b. The effects of varying temperatures for carbon formation during dry reforming experiments.

The specific activities increase with the Ni-content and correlate linearly with the specific metal surface area. After DRM different carbon species were found by TPO as well as TEM investigations of the spent catalysts dependent on the reaction temperature and Ni content: e.g. graphitic layers with and without inclusions of Ni particles, carbon nanotubes and amorphous carbon. In summary, we developed a series of highly active and stable Ni-based catalysts for DRM at 900°C. At these conditions, the catalysts show thermally stable microstructures and high yields in the conversion of CH_4 and CO_2 to syngas.

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OP-17

Biomass Conversion to Synthesis Gas and Hydrogen on Structured Catalysts

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Transformation of fuels (fossil fuel, biofuels) into syngas or hydrogen is one of the most important tasks of catalysis in the energy-related fields. Catalysts comprised of precious metals and/or Ni supported on fluorite or perovskite-like complex oxides with a high lattice oxygen mobility are known to be very efficient and stable to coking in autothermal/steam reforming of a variety of fuels including oxygenates. Monolithic substrates with a good thermal conductivity are promising for providing an efficient heat transfer within the reactor to prevent emergence of hot spots/cool zones deteriorating performance. This work presents results of research aimed on design of such catalysts and characterization of their performance parameters at the pilot-scale level.

Nanocomposite active components were comprised of complex fluorite-like $Ln_x(Ce_{0.5}Zr_{0.5})_{1-x}O_{2-y}$ (Ln = Co, Pr, or Sm, x = 0 - 0.3) or La-Mn-C-rPr-O perovskite-like oxides prepared via modified Pechini route. Precious metals (up to 2 wt.% of Pt, Ru), Ni, Co or $LaNi(Pt,Ru)O_3$ (up to 10 wt.%) were supported by incipient wetness impregnation. Structural features of materials were studied by BET, XRD, and HRTEM with EDX analysis. Oxygen mobility and reactivity of catalysts were studied by temperature-programmed reduction (TPR) using 1% C_2H_5OH in He with subsequent temperature-programmed oxidation (TPOx) by H_2O. Catalytic activity of powdered nanocomposite active components in reaction of ethanol steam reforming (ESR) at short contact times were tested. The oxygen mobility of catalysts in the steady state of ESR was studied using oxygen isotope heteroexchange in both isothermal and temperature-programmed (TPE) experiments (including $^{18}O_2$ and $C^{18}O_2$). The best compositions of nanocomposite active components on the base of extensive lab-scale studies were selected. For preparation of structured catalysts as heat-conducting substrates, fechraloy foil (thickness up to 0.2 mm) and gauze (wire diameter

0.2-0.3 mm) protected by corundum layer were used. Stacked flat and corrugated bands of foil or gauze were winded into the Arkhimed spiral (external cylinder diameter up to 50 mm) forming triangular channels (side 1-3 mm). Another type of design was comprised of a package of corrugated Fechraloy foil plates or Ni-Al foam plates alternatively stacked with gauze sheets. Structured catalysts were prepared by washcoating heat-conducting substrates with slurry of mixed oxides ultrasonically dispersed in water or isopropanol with addition of peptizers and surfactants followed by precious metals/Ni supporting via impregnation. A pilot stainless steel reactor equipped with these catalysts and a front/back thermal shield was connected to the unique electric current heated fuel/water evaporation unit with liquids supplied by the plunger pumps through nozzles, air being fed via a mass-flow controller. As fuels, ethanol, acetone, and glycerol were used. Oxygen content in the feed was varied in the range of 15-20%, H_2O 0-18%, fuel 1-25%, flow rate up to 2 m^3/h (contact times in the range of 5-100 ms).

For all types of fuels, Ru-Co(Ni) and LaNi(Pt,Ru)O_3-containing active components provide the highest performance. Syngas yield increases with the contact time achieving a high level already at $\tau \sim 0.2$ s, which is certainly attractive for the practical application. In typical experiments, at H_2O/fuel ratio ~ 2-3 and inlet temperatures ~ 700°C, H_2 concentration in the exit stream was up to 30-50%. The main byproduct was CH_4 demonstrating occurrence of cracking reactions as well. Addition of O_2 to the feed containing ethanol, acetone or glycerol helps to decrease the inlet feed temperature not decreasing H_2 yield. For such fuels as anisole and sunflower oil, due to their well-known high coking ability, stable performance was obtained only in the case of oxygen addition to the feed. At a proper optimization of contact times and feed composition, no coking was observed for hours-long pilot tests even for sunflower oil as a fuel. No spallation or cracking of the active components supported on metallic substrates was revealed. Hence, monolithic catalysts comprised of heat-conducting substrates with supported complex oxides with a high oxygen mobility promoted by $LaNiO_3$ and precious metals demonstrate a high and stable performance in steam/autothermal reforming of liquid biofuels, including ethanol, acetone and glycerol. This provides new possibilities for transformation of a broad range of complex biofuels (such as products of biomass pyrolysis) into syngas.

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OP-18

Size Effect on Selectivity of NO Neutralization on Pt on Alumina Catalysts

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Industrial boilers as well as heat electric power stations are the major source of environment pollutions. The products of fuel combustion contain a lot of harmful compounds including the most dangerous sulfur oxides, nitrogen oxides and carcinogenic chemical substances. Now two ways of the decreasing of the level of such contaminations are put into practice, namely the improvement of combustion technology and purification of exhaust gases. For the last one the catalytic afterburning of such exhausts is the one of the most practically reasonable approach.

In this work the results of NO adsorption and decomposition study of both model $Pt/AlO_x/FeCrAl$ and ‘real’ $Pt/\gamma\text{-}Al_2O_3$ catalysts by *in situ* X-ray photoelectron spectroscopy (XPS) are presented and compared with isotopic kinetic experiments under static reactor conditions.

One of the most important industrial catalysts ‘Pt on porous alumina’ was modeled by designing of an original system: Pt deposited on a thin alumina film on the surface of a conductive substrate FeCrAl alloy foil [1, 2] . It was shown by STM and XPS that our system has rather rough surface and high stability both in air and solutions treatments. It makes possible to use ‘wet chemistry’ methods for support surface modification and active component deposition from the precursor solutions. The platinum catalysts prepared on the base of this model support were compared with Pt supported on porous alumina with different crystal structure ($Al_2O_3/FeCrAl$ (specific surface area is ~0.06 m^2/g), $\alpha\text{-}Al_2O_3$ (5.3 m^2/g), $\theta\text{-}Al_2O_3$ (110 m^2/g), and $\gamma\text{-}Al_2O_3$ (244 m^2/g)). Both on the surface of model and porous alumina, platinum was deposited from a $H_2[Pt(OH)_6]/HNO_3$ aqueous solution with subsequent reduction in H_2 under close conditions. The size of metal particles on the surface of support is determined by the composition of initial aqueous precursor solutions [3] . Using this method it is possible to control the mean size of particles with good accuracy. To compare our planar models with porous alumina supported catalysts the XPS study of the chemical state of the Pt precursor adsorbed on the surface of different alumina was carried out. It was found that Pt/AlO_x/FeCrAl models are very close to Pt supported on γ-Al_2O_3 system. So this catalyst was used as reference sample for further studies.

Proposed model system was used for *in situ* XPS study under high pressure conditions using both standard Al K_α X-ray source (VG ESCALAB HP, BIC SB RAS, Novosibirsk) and synchrotron radiation (BESSY II, Berlin, Germany) for the NO decomposition study on platinum catalysts depending on mean Pt particle size in the range of pressure from 10^{-5} up to 15 Pa and at temperatures up to 625 K. It was observed that the treatment of samples at these conditions gives rise to N1s features at about ~399 eV and ~403 eV. Adsorbed species were identified as N_{ads} and N_2O_{ads} correspondingly [4]. The main trends of adsorbed layer composition are as follows. The fraction of N_{ads} is rising with temperature increasing and/or NO pressure decreasing; N_2O_{ads} is dominating at low temperature and/or at high pressure. The adsorbed layer composition correlates with mean Pt particle size in the range of diameters from 1.4 up to 4.7 nm. The composition of gas phase products observed for ^{15}NO decomposition on the Pt/γ-Al_2O_3 samples (1.5 – 4.8 nm) under static reactor conditions confirms the observations made for models. It was found that platinum particles with mean size of ~ 2.2 nm show the highest selectivity both in N_{ads} and N_2 formation as compared with either smaller or larger particles.

So platinum catalysts on both model and porous alumina prepared under the same conditions show very similar Pt particle size dependence in adsorbed layer and gas product composition, pointing on the possibility of use of size effect to control selectivity of nitrogen oxide neutralization process. This could be very promising for the resolving of the ecological problems of gas exhaust abatement.

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OS-1

New $Cu_xS/Zn_xCd_{1-x}S$ Photocatalysts for the Photocatalytic Hydrogen Evolution from Na_2S-Na_2SO_3 Aqueous Solutions under Visible Light

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Photocatalytic splitting of water using a heterogeneous photocatalyst has been studied extensively as a potential method to supply hydrogen from sunlight and water. Unfortunately, the efficiency of photocatalytic hydrogen generation over a semiconductor photocatalyst is very low due to the recombination of photoinduced electrons and holes on the semiconductor surface. Using of electron donors, who can react irreversibly with the formed oxygen or photoinduced hole, allows one to enhance the photocatalytic activity in the hydrogen production. In this research we chose Na_2S/Na_2SO_3 system and ethanol as inorganic and organic electron donors for the photocatalytic hydrogen production. H_2S occurs widely in natural gas fields and is produced in large quantities as an undesirable byproduct in the coal and petroleum industry [1].

One of the most well-known semiconductor photocatalysts for hydrogen evolution is the solid solution of ZnS and CdS. In order to achieve the high efficiency for target process many researchers in this field doped photocatalysts by different metals. From a practical point of view, it is desirable to employ low-cost transition metal as co-catalysts for this purpose. Our work is devoted to the investigation of the hydrogen evolution from aqueous solution Na_2S/Na_2SO_3 with using yCuS-$Cd_{0.3}Zn_{0.7}S$ photocatalysts under visible light ($\lambda > 420$ nm).

The photocatalysts were prepared as follows: 0.1 M $ZnCl_2$, 0.1 M $CdCl_2$ and 0.1 M $Cu(NO_3)_2$ with a Zn:Cd:Cu molar ratio of 0.7:0.3:y were mixed in a flask containing 100 ml of 0.1 M NaOH; then 200 ml of 0.1 M Na_2S was added. The reaction system was stirred 20 min. Then the precipitate was collected and centrifuged, followed by washing with deionized water for several times. The catalysts were dried for 15 hours at 70°C. The samples were characterized by XRD method. It has been shown that all samples are solid solutions of CdS and ZnS; in the case of the photocatalyst with the Cu molar content equal to 10% the phase of CuS appears in the XRD patterns (Fig. 1). Photocatalytic hydrogen production from Na_2S/Na_2SO_3 water solutions were conducted in a gas-closed system.

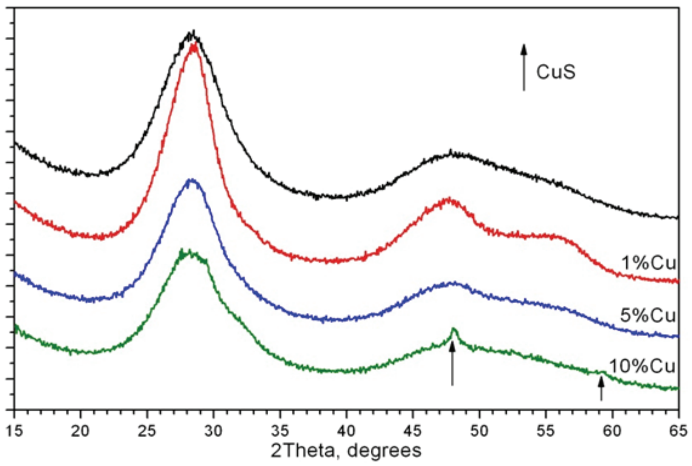

Fig. 1. The XRD patterns of yCuS-Cd0.3Zn0.7S photocatalysts

The photocatalyst powder (0.05 g) was dispersed by a magnetic stirrer in an aqueous (65 ml) containing 0.1M Na_2S and 0.02M Na_2SO_3. The suspensions were irradiated with visible light (λ > 420 nm) through a cutoff filter by a high-pressure mercury lamp.

The effect of copper loading on the reaction rate has been investigated over a set of four photocatalysts of variable metal content in the range of 0-10 mol.%. It has been noted that using CuS as co-catalyst has a promotion effect on the H_2 evolution rate. The reason of this effect is connected with semiconductors' structure. The d orbitals of Cu are generally considered as impurity levels in semiconductor materials [2]. Donor levels from Cu3d orbitals could trap the photogenerated holes, and thus suppress the charge recombination. The reaction rate goes through a maximum of 14.4 μmol/h at y = 0.01 in $yCuS\text{-}Cd_{0.3}Zn_{0.7}S$ and then gradually decreases with rise of copper content in photocatalyst.

The next step of our investigation was the study of the reaction rate *vs.* pH dependences. It was observed that the increase of pH from 8.0 to 9.8 results in a substantial increase of reaction rate (from 43.2 to 54.5 μmol/h). Further increase of solution pH to 14 results in decrease of the reaction rate (from 54.5 to 11.0 μmol/h). This dependence can be explained as follows: when value of pH is high, the target process of the reduction of the proton to the hydrogen atom ($H^+ + e^- = H^0$) is thermodynamically labored. If the pH values decrease, catalyst's decontamination can be realize because of elemental sulphur precipitation.

In conclusions, H_2 can be produced efficiently by photocatalytic splitting of water using Na_2S/Na_2SO_3 system as sacrificial agent and a solar light-simulating source. The best results were obtained for 1% $CuS/Cd_{0.3}Zn_{0.7}S$. The quantum efficiency was 23.5%, which is a large value for a process on a catalyst containing no noble metal.

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OS-2

Surface Dynamics of the Intermetallic Compound Pd_2Ga and its Catalytic Properties in Liquid Phase Alkyne Hydrogenation

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Pd based catalysts are widely applied catalysts for hydrogenation reactions and are in particular highly effective for the semi-hydrogenation of the C-C-triple bond in gas and in liquid phase. The enhanced selectivity of Pd towards suppressed alkene hydrogenation originates from an *in situ* modification of Pd by C in the sub surface region [1]. It is well-known that Pd-based catalyst can operate in a selective as well as in an unselective manner favoring formation of the alkene and alkane respectively, which is reasoned by the limited stability of the Pd-C phase. Also efficient modified catalysts like Pd-Ag alloys [2] or $Pd/CaCO_3$ poisened with $Pb(OAc)_2$ (Lindlars catalyst) [3] have been developed, these catalyst are not always necessarily stable and selective under reaction conditions and novel material are still required.

The intermetallic compound Pd_2Ga was shown to be a selective catalyst for the semi-hydrogenation of acetylene, which was reasoned by the partial isolation of active sites and a, compared to Pd, strongly intrinsically modified electronic structure [3,4]. Its d-band centre is shifted away from the Fermi level. In this work, the structural and electronic properties of unsupported powdered Pd_2Ga were investigated in different environments and correlated with its catalytic properties for the liquid phase hydrogenation of phenylacetylene. While the bulk of this material provides a high stability, it was found that the electronic structure of the surface of the intermetallic compound depends strongly on its pre-treatment and the chemical environment. The surface is highly sensitive against traces of oxidizing agents, leading to a fast decomposition into Ga oxide and a Pd enriched surface. Additional mechanical load promotes further Ga segregation from the bulk and the subsurface, leading quickly to a disparity between the bulk and the surface structure. By a high-temperature treatment in H_2 atmosphere, an almost clean surface of Pd_2Ga can be obtained. Compared to elemental Pd, the hydrogenation activity of Pd_2Ga is significantly lowered, which is reasoned by the intrinsic d-band shift away from the Fermi edge.

The intermetallic surface cannot be stabilized under liquid phase hydrogenation conditions but is subjected to oxidative decomposition in presence of small traces of O_2 and H_2O, leading to a gradual increase of the rate of consumption of phenylacetylene. By applying very inert conditions before and during reaction this decomposition can be suppressed. However, without a passivation layer also the bulk material of Pd_2Ga gets attacked by phenylacetylene during reaction leading to further increase of reaction rate. The controlled strong manipulation of the crystal and the electronic structure by alloying a noble metal with a less noble metal and thus a controlled modification of the adsorption properties is feasible, but it is accompanied with a significantly decreased stability and is not applicable under practical conditions.

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OS-3

Study of Pt Catalysts Supported on Different Carbon Materials in the ORR in PEMFC

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The performance of Pt/C catalysts in oxygen reduction reaction (ORR) is of great importance due to their use in polymer electrolyte fuel cell (PEMFC). The increase in the ORR activity of Pt/C catalysts results in the decrease of the Pt load in the cathode of PEMFC which reduces much the cost of PEMFC. The effectiveness of Pt/C catalysts in ORR in PEMFC is dictated by intrinsic kinetics of the ORR on Pt, oxygen and water transport inside electrode layer and catalyst grain, and proton transport to the active sites. These phenomena are affected by the properties of carbon support. Its optimal porous structure and morphology should minimize transport losses as well as enhance the ORR kinetic.

In this work, the series of Pt/C catalysts were synthesized and studied in ORR in PEMFC. The catalysts were differed in the Pt content (20-60 wt.%), porous structure and morphology of carbon supports (Vulcan XC-72, Sibunit-1562, Black Pearls 2000 and Ketjenblack DJ-600). The Pt size in the catalysts as obtained by CO titration were in the 2-6 nm range depending on the Pt content. Membrane-electrode assemblies based on the catalysts were synthesized and tested in PEMFC. Their activities in ORR in PEMFC were obtained according to Gasteiger et al. [1]. As compared to commercial 20 wt.% Pt/Vulcan XC-72 catalyst, several times higher activities were found for the new Pt/Sibunit-1562 catalysts. The improved performance of the Sibunit-based catalyst was attributed to the higher dispersion of Pt and improved mass transport inside a grain of Sibunit-1562 carbon support as well as in cathode layer. The effects of porous structure and morphological properties of the carbon supports, Pt content in the catalysts, and Pt load at the cathode on the activities in ORR are discussed.

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Stability of Electrocatalyst Materials – a Limiting Factor for the Deployment of Electrochemical Energy Conversion?

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Continuous growth of energy consumption and concomitant fast depletion of fossil fuel resources triggered research, development and deployment of alternative renewable solutions. Thus, electrochemical reactors like electrolyzers and fuel cells have attracted much attention due to the possible application for clean energy conversion and storage [1]. Since their real implementation has to be technologically reliable and economically efficient in terms of costs and performance, a lot of work has been focused on the search for catalysts with lower noble metal content but still high activities. However, although having equal importance for long-term operation, the stability of electrode materials has been widely neglected in the development process. As a consequence, a lot of novel catalyst materials with only limited industrial relevance, have been proposed recently.

In our group stability and activity are considered to be of equal importance and are always investigated in parallel. Therefore, we have developed a unique *in-situ* technique for comprehensive catalyst performance studies. Activity screening of electrocatalyst materials by a Scanning Flow Cell is complemented by downstream elemental analysis of trace amounts of metals in the electrolyte due to catalyst degradation by an Inductively-Coupled-Plasma Mass Spectrometer. Obtained results reveal first of all the different amounts of noble metal catalyst dissolution in ppt concentration during different operational conditions [2–4]. Moreover, conclusions can be drawn on dissolution mechanism due to the full time resolution of the technique. So for instance, while significant loss of platinum and rhodium is observed during the transient processes of oxide formation and reduction, gold constantly dissolves at high anodic potentials. In the current work, the study will be extended to other noble metals of the platinum group, which cover the most widely employed materials in acid water electrolysis and low-temperature fuel cells.

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OS-5

Catalytic Hydrodeoxygenation of Plant Fatty Acids Derivatives

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Nowadays it becomes more perspective to produce engine fuels from the renewable sources. The first direction of the present work is devoted to the biodiesel hydrodeoxygenation process study. The biodiesel is a mixture of methyl esters of fatty acids (FAMEs). In spite of a number of its ecological advantages, biodiesel cannot be used in diesel engines without modernization of the engine. The main reason for the quite low operating characteristics of biodiesel is high oxygen content due to the presence of ester groups (11-12 wet.%) in its components. Therefore the FAMEs can be used as a fuel for diesel engines only in a mixture with the hydrocarbon fuels.

The main aim of the present work is a development of biodiesel hydrodeoxygenation process in order to obtain high - cetane hydrocarbons - "green diesel". It should be noted that in contrast to the oil refining it is desirable to use non-sulfided catalysts in this process because of the low sulfur content in the biodiesel. Therefore the development of the new catalysts for biodiesel hydrodeoxygenation (HDO) is also the important aim of the present work.

The reaction was carried out with the commercial biodiesel produced from the colza oil. The results of biodiesel hydrodeoxygenation study showed that the most active catalysts are Rh/CeO_2-ZrO_2 and Ni-Cu/CeO_2-ZrO_2. The biodiesel methanization at the hydrodeoxygenation process is the feature of the nickel-based catalysts. Introduction of copper into the nickel catalysts increases the temperature of the methanization process started between 300-320 and 390-410^{0}C. The main products obtained at 270-400^{0}C and 0.5-1.5 MPa of H_2 were linear hydrocarbons C_{14}-C_{17} .

The second direction of this work is research and optimization of plant fatty acids hydrodeoxygenation process in order to obtain fatty alcohols. Fatty alcohols are very important commodity chemicals. They are valuable products used in detergents industry, cosmetic, and pharmaceutical applications.

The reaction was carried out with the oleic acid in presents of Rh-B-Sn/Al_2O_3 and Co-B-Sn/Al_2O_3. The results of oleic acid hydrodeoxygenation showed that the main products obtained at 250-400^{0}C and 80 MPa of H_2 were oleyl alcohol (selectivity up to 40%), alkanes (selectivity up to 45%), and undesirable product – wax. Therefore the selection of the optimal condition for minimal wax yield is also the important aim of the present work.

The variation of the process conditions and nature of the catalyst modifier enabled to produce different hydrocarbon products. The obtained experimental data on the examined catalysts stability and selectivity makes it possible to make the conclusions about a possibility of the given process industrial realization.

OS-6

Catalytic Upgrading Valeric Acid to n-Nonane as Promising Way to Produce Green Diesel Components

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Recent studies have identified 12 promising biomass derivatives based on their production costs and the potential of these molecules to serve as building blocks for the development of bio-refinery processes [1]. Levulinic acid, one of the biomass derivatives, can be produced using dehydration of carbohydrates, obtaining by lignocellulosic biomass hydrolysis [2]. This acid has the potential to be a platform molecule for the production of fuels components [3] and valuable chemicals [4]. However, levulinic acid, as all the biomass derivatives, has hydroxyl and carboxylic groups that complicates control acid reactivity and direct the conversion to targeted compounds. A partial reduction of the oxygen content of the molecule leads to less reactive intermediate, valeric acid, which further can be upgraded to n-nonane, green diesel component (Fig. 1). Herein we propose a new strategy to converse valeric acid into n-nonane. One-pot process of valeric acid ketonization followed by 5-nonanone deoxygenation into n-nonane over Pt(Pd)/M_xO_y bifunctional catalyst can be considered as a more attractive way to produce green diesel components.

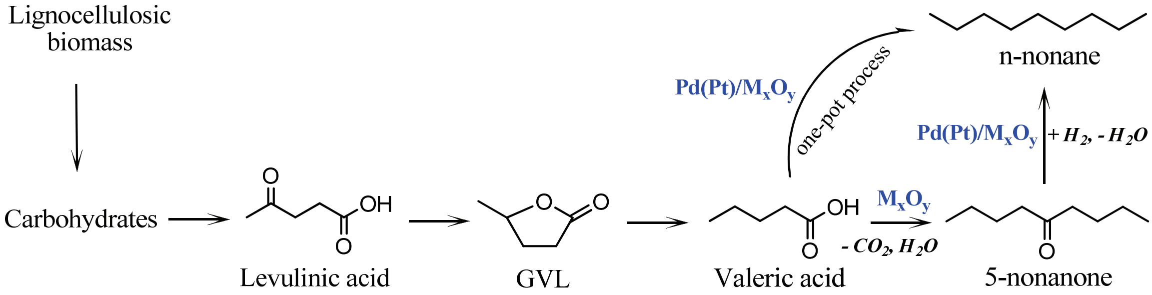

Fig. 1. Scheme of lignocellulosic biomass conversion into n-nonane.

The aim of our work was to design the bifunctional catalyst and optimal reaction conditions for one-pot process and carry out the process, using data obtained. To reach the aim a search of active and stable catalyst and optimal conditions for ketonization and deoxygenation was performed individually. The ketonization was carried out in the fixed bed flow reactor in the vapor phase at 573-678 K under hydrogen stream at 1 atm with the flow rate of 30 cm^3/min. Before the reaction the M_xO_y catalyst (m = 0.5 g, fraction = 0.25÷0.5 mm) mixed with quartz (m = 3g, fraction = 1.0÷1.25 mm) was heated in hydrogen stream to reaction temperature. Then pure valeric acid was fed using a syringe pump with liquid hourly space velocity (LHSV) = 0.33-1 cm^3/(g·h). Catalyst was kept in reagent flow at reaction temperature for 1 hour, and then the condensable products were collected in the trap with liquid nitrogen through 2 hours. The deoxygenation was carried out the fixed bed flow reactor at 573-628 K under hydrogen stream at 6-12 atm with the flow rate of 100 cm^3/min. Before the reaction the Pt(Pd)/M_xO_y catalyst (m = 3.4g, fraction = 0.25÷0.5 mm) mixed with quartz (m = 2.4g, fraction = 1.0÷1.25 mm) was heated in hydrogen stream to reaction temperature. Then 10 vol.% solution of 5-nonanone in hexane was fed with liquid hourly space velocity (LHSV) = 7.3 cm^3/(g·h). The reaction products were identified by Agilent Technologies 7000 GC/MS Triple Quad using silica fused capillary column Agilent HP-5ms (30m/0.25mm/0.25µm, USA). The product contents were determined by GC on Stabilwax-DA (50 m/0.32 mm/0.5µm, USA). The catalysts were analyzed by XRD, HRTEM, XPS, *in situ* FTIR, *in situ* UV-Vis.

It was found that ZrO_2 и CeO_2/ZrO_2 were the most active catalysts under optimal conditions (T = 628 K, LHSV = 0.5 cm^3/(g·h)) in ketonization of valeric acid to 5-nonanone, showing yield of 76 % with 79 % selectivity. Then these oxides were used as supports to synthesize Pt(Pd)/M_xO_y catalysts of various metal dispersion for deoxygenation of 5-nonanone to n-nonane. Pt(Pd)/M_xO_y catalysts with the highest dispersion showed similar yield of 85-90 % and selectivity of 85-90 % under T = 628 K and P = 6 atm. Pd/ZrO_2 catalyst was tested in one-pot process ketonization/deoxygenation of valeric acid to n-nonane under T = 628 K and P = 6 atm. Using data obtained by physico-chemical methods a correlation between catalytic activity and structural and electronic properties of catalysts was determined.

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OS-7

Aerogel Synthesis of Nanocrystalline Binary MO_x/MgO Systems for Catalytic and Energy Storage Applications

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The binary nanocrystalline MO_x/MgO systems (where M = V, Co, Fe, Ce etc.) have attracted much attention due to their unique physical characteristics, morphology and enhanced catalytic properties in various processes. Nanoscale oxides are prospective for many applications in electronics, catalysis, ceramics, nanostructured composites or energy storage materials. Authors developed the procedure for the synthesis of mixed hydroxide/oxide systems (based on aerogel preparation of $Mg(OH)_2$) to be considered as candidates for use in the medium-temperature chemical heat pumps [1].

The synthetic procedure described in details in our earlier papers [2] allowed us to obtain the nanocrystalline mixed VO_x/MgO catalysts within the wide range of V loadings (1-25 wt.%). The preparation is based on aerogel technique which comprises the hydrolysis of a mixture of vanadium and magnesium alkoxides followed by gelation and subsequent drying in autoclave at supercritical conditions. It was demonstrated that such method permits one to provide the quite uniform distribution of the active component (VO_x) throughout of MgO nanoparticles of about 2-5 nm in size. Aerogel VO_x/MgO catalysts were found to possess superior activity in the oxidative dehydrogenation of propane as compared to samples prepared by conventional methods [3].

The mentioned technique has been recently adopted for the synthesis of binary MO_x/MgO systems with various modifying additives (M = lithium, calcium, cobalt, nickel, iron, copper and cerium). A series of synthesized mixed hydroxides M-$Mg(OH)_x$ and oxides MO_x/MgO (obtained by the following T-programmed decomposition of the corresponding hydroxides) have been characterized by a number of physicochemical methods (XRD, TGA, BET, and HRTEM with EDX analysis). It was found that the specific surface area of M-$Mg(OH)_x$ hydroxides varies within the range of 400-800 m^2/g depending on nature of M, whereas the pore volume for all exceeds 1 cm^3/g.

Microscope images of binary Co-MgO and Cu-MgO samples (containing both 10 at.% of the active metal, Co or Cu) are presented on Fig. 1.

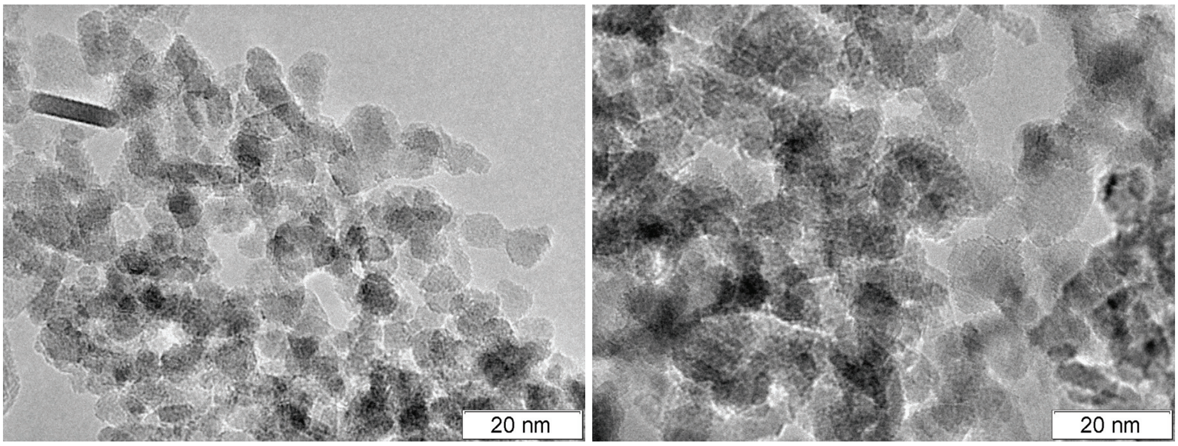

Fig. 1. TEM images of Co-MgO (A) and Cu-MgO (B) binary oxides heated at 500°C.

According to TEM (combined with EDX analysis) data, the chemical composition and morphology of synthesized materials is sufficiently uniform. The size of primary oxide particles does not exceed 20 nm. Similar situation was found to majority of prepared oxides.

The experimental results on study of correlation between active sites structure and primary particles size with thermal effects taking place during the decomposition of hydroxides; as well as the catalytic properties of prepared nanocrystalline MO_x/MgO systems in oxidative dehydrogenation, and their structural and textural peculiarities will be discussed in details.

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OS-8

Regenerable CO_2 Sorbent for Thermochemical Energy Storage Systems

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Installing energy storage systems (ESS) for wind turbines power can bring many benefits to both power grids and wind power developers. Considering stochastic nature of wind, electric power generated by wind turbines is highly erratic and may affect both the power quality and the planning of power systems. ESS should play a key role in wind power applications by controlling wind power plants output and providing ancillary services to the power system, and therefore, enabling an increased penetration of wind power in the system [1].

One of the most promising among ESS is the system where electricity generated by power station can be utilized in water electrolysers to produce hydrogen [2].

$$2H_2O \xrightarrow{electrolysis} 2H_2 + O_2$$

Since the storage and the transport of hydrogen are dangerous and still very expensive it is reasonable to produce less explosive fuel, e.g. methane, which can be obtained in the chemical reaction between hydrogen and CO_2 captured from air by Sabatier process [3,4]:

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O.$$

Important advantage of this system is the possibility of a prolonged and relatively safe storage of energy carrier (methane) and the ability to transport it over long distances that is 3-5 times cheaper than the transport of electricity [1]. Also such methane producing factories can be used as gas stations for gas engine vehicles.

Anthropogenic CO_2 can be used as a valuable feedstock for the production of fuel in such systems. Carbon dioxide capture from ambient air is challenging because of very low concentration of CO_2 in air (~ 400 ppm) and the necessity to operate in the presence of moisture excess at ambient temperature and pressure. The most developed technologies for direct CO_2 capture from air are based on carbon dioxide absorption by aqueous solutions of organic amines such as MEA [5] and aqueous solutions of alkali carbonates [6]. Solid inorganic chemisorbents are not currently used for CO_2 capture from air due to very low carbonation rates [7]. However, it is possible to overcome this problem by deposition of the solid chemisorbent in porous media with high specific surface area. For instance, composite materials prepared by potassium carbonate deposition on various mesoporous solids were shown to be very promising sorbents for CO_2 capture from wet flue gases [8-10].

Here we present a novel approach to direct CO_2 capture from ambient air using a regenerable K_2CO_3/γ-Al_2O_3 sorbent. It was prepared by impregnation of mesoporous alumina pellets with K_2CO_3 aqueous solution. The sorbent has been successfully tested under conditions of the temperature swing adsorption (TSA) cycle. It was shown that the increase in the regeneration temperature (T_{reg}) from 150-200°C up to 250-300°C leaded to augmentation of CO_2 sorption capacity up to 4.0-4.9 wt.%. The additional amount of CO_2 is desorbed due to decomposition of nanodispersed $KAlCO_3(OH)_2$ crystalline phase, which is likely to produce highly reactive K_2CO_3 species as a result of heating.

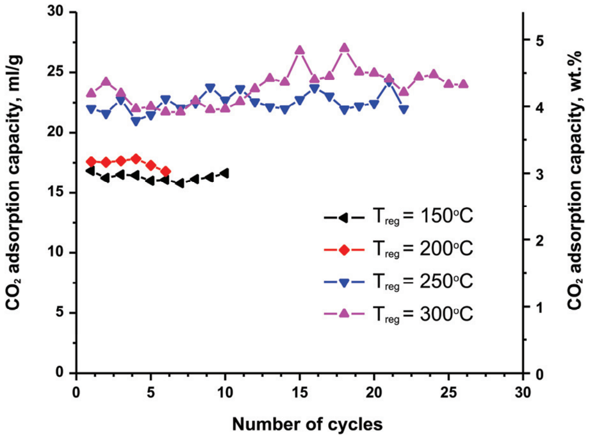

Fig. 1. CO_2 sorption capacity in TSA cycles with different T_{reg}.

The stability of the sorbent has been demonstrated for over 100 cycles of sorption regeneration with the regeneration temperature of 150-300°C. K_2CO_3/γ-Al_2O_3 sorbent should be considered as a promising material for air capture technology. These results are of interest for the capture of air-borne CO_2 with subsequent renewable methane production in thermochemical systems for storage and utilization energy of wind.

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OS-9

Ultrasound-Assisted Activation of Aluminum Based Alloy Particles for Electrocatalytic Applications toward Hydrogen Evolution Reaction

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To date electrolysis of water is one of the most common "non hydrocarbon consuming" ways of high purity grade hydrogen production. Even though it accounts only for about 4% of globally produced hydrogen, electrolytic water splitting may become primary source of hydrogen. Here we report the method of metal alloy surface activation for hydrogen generation.

The method is based on utilizing of high-intensity ultrasound (US) for creation of electrocatalytically active interface of aluminum based alloys. US of high intensity, while acting on metal alloy, is changing its surface morphology, distribution of the elements/compounds, as well as responsible for a formation of new phases. Through the adjustment of sonication media, duration of US treatment, and drying procedure, aluminum based alloy interface with enhanced electrocatalytic properties is formed. Namely, reduction of overpotential (-0.6 V) at which hydrogen evolution reaction (HER) occurs, higher current output (147.5 mA/cm^2) at fixed overpotential (-1.1 V), as well as improved exchange current density values (2.26 mA/cm^2) are achieved. Morphology and elements/compound redistribution of modified alloys were studied with help of scanning electron microscopy, powder X-ray diffraction technique, electron dispersion X-ray spectroscopy, as well as temperature programmed technique and inter-pore / particle diffusivity measurements by ^{129}Xe NMR. Electrocatalytic activity of aluminum based alloy particles toward HER was investigated by linear sweep voltammetry.

High Surface Area Carbon Materials as Electrodes for Electric Double Layer Capacitors

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Electric double layer capacitors (EDLC) are type of electrochemical storage devices suitable as alternative or complement to other devices such as battery or fuel cells. The operation principle of EDLC bases on the charge separation on the interface between electrode surface and electrolyte. Carbons are one of the promising materials for the electrode construction in capacitors due to their highly extended surface area, which allows to store increased amount of charge [1]. Various carbon materials have been intensively investigated as electrode materials for EDLC because of their attractive electrochemical performance and capacitive characteristics [2-4]. Carbons prepared from biomass precursors besides high surface area (more than 3000 m^2/g) are relatively cheap due to the low-cost and available resources.

Carbons presented in this work were prepared from rice husk [5,6]. These materials possess appropriate characteristics for application in EDLC such as high surface area and suitable micro-/mesopores ratio. Textural characteristics have been investigated by different physical methods (BET, XPS, SEM). Investigation of the electrochemical properties was carried out by cyclic voltammetry and chronopotentiometry in aqueous electrolytes. It was shown that the gravimetric capacitance depends on surface area of the carbons (Fig. 1).

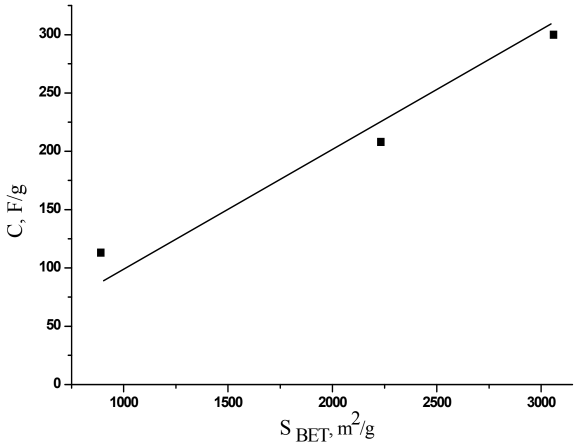

Fig. 1. Dependence between carbon surface area and gravimetric capacitance.

OS-10

In order to improve capacitive characteristics, carbons have been modified. Modification of the carbon surface by deposition of the conductive polymer, polyaniline, leads to the increasing of the electrode capacitance: carbon with 2230 m^2/g surface area possesses 183 F/g gravimetric capacitance while deposition of polyaniline increased capacity up to 309 F/g at current density 1 A/g.

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Crystallographic and Thermodynamic Approach in the Choice of Catalyst Systems

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High catalytic activity of the electrode material is of great importance for low-temperature fuel cells (FC). A list of the investigated catalysts for the electrochemical reaction of hydrogen-oxygen FC includes metals of Group VIII of the Periodic table and their alloys with each other and with the metals VI, VII, and I groups, silver, chalcogenides of transition metals, tungsten carbide, nickel boride, charcoal, activated spinels, cobaltite nickel, nickel oxide with addition of lithium oxide, cobalt porphyrins, phthalocyanines of iron. The most effective catalyst is platinum. It has a high thermodynamic stability in aggressive substances. Replacing platinum or decrease its share in the catalyst is an urgent task. The development on creature of bi- and trimetallic systems on the basis of PtM1/C and PtM1M2/C (M1, M2 – transition metals) allows to reduce platinum content in the catalyst system. Stability of the catalyst system in FC depends on the interface defects on the border of the two metals. For the synthesis of bimetallic catalyst is expedient to use metals with face-centred and hexagonal closely packed lattices which correspond to the face-centred lattice of platinum. The combination of two face-centred metals may for various crystallographic planes, and a combination of hexagonal closely packed metals and platinum may along the [111] direction of the platinum. The crystallographic parameters of metals (Pt, Pd, Ir, Rh, Re, Co, Ni, Fe, Cr, Ag, Ru, Os, Au, Cu), which are interesting for the scientific literature as the components of catalyst system of FC, are used for calculation of the ratio of the parameters and areas of figures, which can be on abutting joint metals by formation of bi-catalyst. The calculation showed that of the 13 studied metals for the synthesis of bimetallic catalyst based on platinum are suitable the three face-centred metals: Pd, Ir, Rh and three hexagonal closely packed metals: Re, Os, Cr. At a certain orientation of the crystallographic planes interest Au, Ag, Ni. Four (Pd, Ir, Rh, Os) of these nine metals are representatives of the platinum group. Re, Au and platinum are in one period, Ni is in the same group, Cr is similar to Re and Os lattice parameters as Ag to Au. Using the software package HyperChem 6.0 and Minkrist-site data models bi-catalyst structures across several unit cells were constructed. Their energy stability will explore by the methods of computer modeling later.

The structure and chemical composition of the surface layer, the correspondence between the chemical properties of the catalyst and reactants determine the efficiency of a heterogeneous catalyst according to the theory of heterogeneous catalytic processes (which include electrochemical reactions). On presentation of the theory of the intermediates, the intermediate complexes of catalyst with reagents are formed during catalysis. They disintegrate into products and catalyst later. The changes of the thermodynamic potentials of stages of formation and destruction of the intermediates between the initial materials and the catalyst should be similar and equal to half of the thermodynamic potential of the overall reaction. The overall reaction is the oxidation of hydrogen, changes standard thermodynamic potentials for which are: ΔH^0_{298}=-285.8 kJ; ΔG^0_{298}=-237.2 kJ. Intermediates are the hydrides (the anode) and oxides (the cathode) of the metal catalysts. If the changes the standard thermodynamic potentials reactions of formation and destruction of intermediates in presence metal composite, kJ: $\Delta H^0_{298} \approx -140$, $\Delta G^0_{298} \approx -120$, should this metal choose as the catalyst. Thermodynamic calculations (by the published data on the phase of the compounds) have shown that if the catalysts are combined by certain pairs in fuel cell, can be used Pd, Ni, Cr for the oxidation of hydrogen, and Pt, Pd, Rh, Ir, Os, Ni, Co, Cu, Re are suitable for the reduction of oxygen (see table below). Quantum kinetics calculations of activity of catalyst intermediate complexes with reagents allow one to do more accurate choice of the catalyst system for low-temperature fuel cells [1].

Table – Change of the thermodynamic potentials of reaction for the catalytic systems

№	Reaction	ΔH^o_{298}, kJ/mol H_2O	ΔG^o_{298}, kJ/mol H_2O
1	$2Pd_2H + PdO = H_2O + 5Pd$	**-104.1**	**-117.6**
2	$4NiH_{0.5} + NiO = H_2O + 5Ni$	-10.9	-119.9
3	$CuH_2 + CuO = H_2O + 2Cu$	-117.2	-
4	$2Pd_2H + PtO = H_2O + 4Pd + Pt$	**-148.5**	**-156.9**
5	$4NiH_{0.5} + CoO = H_2O + 4Ni + Co$	-11.7	-120.8
6	$4NiH_{0.5} + CuO = H_2O + 4Ni + Cu$	-107.1	-201.9
7	$2NiH + CuO = H_2O + 2Ni + Cu$	-	-124.,3
8	$NiH_2 + CuO = H_2O + Ni + Cu$	-	-121.3
9	$2Pd_2H + RhO = H_2O + 4Pd + Rh$	-	-135.5
10	$Cr_7H_2 + CuO = H_2O + 7Cr + Cu$	-126.8	-
11	$4Pd_2H + PtO_2 = Pt + 8Pd + 2H_2O$	**-152.168**	**-161.08**
12	$6Pd_2H + Rh_2O_3 = 2Rh + 12Pd + 3H_2O$	-	-133.2
13	$6Pd_2H + Ir_2O_3 = 2Ir + 12Pd + 3H_2O$	-	-147.4
14	$4Pd_2H + IrO_2 = Ir + 8Pd + 2H_2O$	-84.08	-144.33
15	$8NiH_{0.5} + IrO_2 = Ir + 8Ni + 2H_2O$	-115.08	-273.03
16	$2Cr_7H_2 + IrO_2 = Ir + 14Cr + 2H_2O$	-134.78	-
17	$8Pd_2H + OsO_4 = Os + 16Pd + 4H_2O$	**-121.31**	**-128.13**
18	$8NiH_{0.5} + ReO_2 = Re + 8Ni + 2H_2O$	-38.73	-143.98

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Computational Study of O_2 Interaction with Gas-Phase and SiO_2 Supported Ag_3 and Ag_4 Clusters

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Silver clusters containing just few atoms, Ag_n ($n<10$), demonstrate high catalytic activity in number of oxidation reactions or reactions for which oxidation step is very crucial. As most important reactions the propylene epoxidation [1] and the selective catalytic reduction of NO by hydrocarbons [2] can be mentioned. The key factor determining high activity of silver in oxidation processes is its ability to activate molecular oxygen. Up to recent years main conclusions on interaction of O_2 with silver clusters is mostly based on experimental and theoretical studies of gas-phase Ag species. At the same time investigations of the catalytic activity of supported Ag clusters of subnanometer size remain relatively rare case, despite the known fact of dramatic support effect on chemical properties of adsorbed clusters [3]. Present theoretical study aims to fill partially this lacuna focusing on how oxygen interacts with free and silica-supported silver clusters.

We applied an all-electron scalar relativistic density functional method to explore interaction of O_2 with unsupported and supported on a dehydroxylated silica surface Ag_3 and Ag_4 clusters. To model SiO_2-containing systems we used an accurate hybrid approach of embedding QM cluster in elastic polarizable environment described by molecular mechanics [4]. Since defect-free silica surface is nonreactive, we modeled isolated paramagnetic defect – nonbonding oxygen, ≡Si-O• (NBO) featuring strong bounding with Ag clusters [5].

Gas-phase Ag_3 cluster is characterized by open-shell electronic structure resulting in about three times larger binding energies with O_2 ($69 \div 109$ kJ/mol) compared to closed-shell gas-phase Ag_4 cluster ($21 \div 41$ kJ/mol). Adsorption of oxygen molecule with O-O bond parallel to the cluster edge is the most preferred on both silver clusters. The oxygen negative charge in O_2/Ag_n systems ($-0.30 \div -0.35e$) and the O-O bond length (~133 pm) point out the existence of O_2 in a form close to superoxide O_2^-. The energy gain upon adsorption of O_2 in dissociative form on Ag_3 and Ag_4 clusters is modest (39 kJ/mol). The activation barriers of O_2 dissociation

– 256 kJ/mol for Ag_3 and 184 kJ/mol for Ag_4 – shows opposite trend to stability of O_2/Ag_n complexes.

Spin state of silver trimer and tetramer is reversed upon trapping of silver clusters by paramagnetic NBO defect of SiO_2 surface: Ag_3/SiO_2 and Ag_4/SiO_2 systems become closed-shell and open-shell, respectively. Transfer of electronic density from silver clusters to NBO center is ~0.45e, thus, supported Ag_n clusters is positively charged. In analogy to free clusters, interaction of O_2 with Ag_3/SiO_2 system with even-number of electrons is weak. The adsorption of O_2 is energetically favorable (~12 kJ/mol) only in case of O_2 binding to Ag species via one oxygen atom. The energy of two-end coordination mode of O_2 is close to zero, while formation of dissociative O_2 complex on Ag_3/SiO_2 cluster is unfavorable. On the contrary, adsorption of O_2 on Ag_4/SiO_2 complex is the most favorable in dissociative form with binding energy ~120 kJ/mol. The most stable non-dissociative O_2 form at supported Ag_4 cluster (97 kJ/mol) is two-end superoxide-like form accompanied by transformation of Ag_4 moiety from rhombus into tetrahedra. The lowest calculated activation barrier of O_2 dissociation on Ag_4/ SiO_2 complex (181 kJ/mol) is close to that for gas-phase Ag_3 cluster.

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OS-13

Investigation of Promoted Magnetite Catalytic Prospects for Cleaning Exhaust Gases from Carbon Monoxide

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Oxygen-deficient complex iron oxide, known as magnetite (Fe_3O_{4-X}, spoken later as ODM), has been recently investigated. When synthesized under certain conditions, ODM is able to self-arrange structural defects within its spinel-type lattice. Contribution of various physic-chemical factors to the ODM formation and properties has also been investigated. In particular, the ability to repeatedly adsorb/desorb atomic oxygen from the air may prove valuable in chemisorption. In that case, we believe that ODM may act as a promising catalyst for purification of exhaust gases of different origin, mainly from CO, which is successfully converted to CO_2. ODM is not toxic and shows limited biodegradability. Moreover, ODM is not sensitive to the known catalyst poisons (SO_2, NO_X), acting as an effective oxidant by itself. Because structural defects are proved to periodically regroup and even rearrange, regardless of conditions, the ability of ODM to self-regenerate is still under investigation. ODM may act as a catalyst itself or may be incorporated into an active phase of more complex catalyst, or may function as a part of block media (carrier), depending on the chosen applications. In previous studies, it was calculated and experimentally confirmed, that partial substitution of iron ions in the ODM crystal lattice with other transient metal ions (and their combinations, up to 27% in total) makes no influence to the structure and properties of ODM.

While investigating ODM promotion pathways, the authors have found out that the synthesis is well-described by the modified Wagner model. First, a range of solid solutions, mainly consisting of a mixture of simple and complex oxides, is formed, and then local crystallization centers with ferrite grains appear, both processes can be controlled, as shown below. The described transformations were confirmed by SEM, XRD and elemental analysis.

Synthesis of the catalyst was performed via thermal decomposition of fine crystalline mixture of organic salts of iron and metal promoters (4:1 wt.). Fine crystalline organic ammonium salts in various proportions were added to the mixture, acting as fluxes, to control the atmosphere in the area of synthesis. The temperature and time of calcination, as well as flux quantity and composition, were varied. The samples were dispersed and heated in the muffle oven for an hour prior to the desired temperature and calcinated at the same temperature for up to 24 hours. After calcination, the samples were cooled down in the oven for 1 hour and then unloaded into a desiccator with a mixture of silica and zeolite filled with high purity nitrogen or argon, where they were naturally cooled down to room temperature. Cooled samples were dispersed into 120 micron particles and tested for running the catalytic conversion of CO in a flow reactor, or on the above-mentioned analytical equipment, used to control the methods and quality of the samples. Analysis of the diffraction data and microscopy allowed us to recommend calcination at temperatures up to 900° C. Furthermore, optimal quantity and composition of flux allows us to avoid blowing inert gas through the oven for the entire time of synthesis, which simplifies the process and reduces its expenses. All samples being analyzed confirm that the structure and composition are close to pre-calculated.

Because of cation interdiffusion within the mixture of complex oxides (Fe_3O_4 + Me_3O_4), formed within first hour, rapidly growing coral-like structure appears, composition confirmed by elemental analysis. The use of more complex fluxes allowed the authors to control growth and to improve the structure of the product, so that self-arrangement took place, and the target system behaved like an inorganic foam polymer (pore size - 200 nm or less) and looked like HPCM. After 2 more hours of calcination, ferrite grains started to form and local planes began to sprout in one or two directions.

In particular, the study of the iron-manganese-oxygen system confirms formation of that coral-like intermediate structure consisting of Fe_3O_4 and Mn_3O_4, and locally crystallized franklinite ($MnFe_2O_4$). Moreover, when interpreting diffraction patterns of this system, in addition to the above compounds, a slight amount of simple oxides of Fe and Mn is present, although it was not visually confirmed. Similar results were obtained for the systems containing cobalt, nickel, copper and zinc as the metal-promoter. It is worth mentioning, that intermediate also exhibits the desired catalytic activity for CO oxidation process, therefore said mixture is quite effective, regardless of the content of the target product - ferrite. Structure and properties of the studied systems containing complex oxides of iron (ferrite), can be considered both at the macro level - as HPCM, and at micro-level - as nanoreactors.

To assess the effectiveness of the carbon monoxide conversion the reactor was purged with mixture of carbon monoxide, carbon dioxide and humidified air to simulate the composition and conditions of the flue gases in the catalytic cracking, gas flow rate and the temperature (600-700° C) were varied. In terms of the monolayer, the conversion in preliminary tests was 60%. Further tests are carried out in a fluidized catalytic conversion layer, catalyst self-regeneration occurred as expected.

Catalytic Oxidation of Methane Traces in NGVs Engines Exhaust: Problems and Perspectives

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Natural Gas Vehicles (NGVs) is a very perspective development that could solve many of problems connected with usage of traditional gasoline and diesel vehicles. Among them is the decrease of carbon dioxide, soot and nitrogen oxides concentrations in the exhaust of natural gas engine. Moreover, natural gas engines is said to be more energy efficient than traditional ones. However this type of engine could not be used massively because of the problem of unburned methane combustion.

Methane is the main component of natural gas, the most stable hydrocarbon and therewith is the dangerous greenhouse gas. Its pollution of the atmosphere can cause severe damage to the world ecology, so, in consideration of unburned methane existence in the NGVs exhaust there were developed strong restrictions to the methane concentration in exhaust. To meet these conditions very efficient catalytic methane combustion is needed. It is considered that the most popular and promising catalyst for this process is Pd supported on alumina. Such catalysts demonstrate the highest activity towards methane combustion among all known precious metal catalysts, but there is a still unsolved problem of palladium deactivation during the reaction. It is said that palladium inhibition is caused by water vapor which is not only the combustion reaction product, but is also a component of gas-oxygen mixture [1-4]. There is some contradictory information in the literature about the possibility of palladium stabilization via addition of some promoters such as Ni, Co, Pt, Sn oxides to the catalyst composition [5-7]. Moreover, methane combustion reaction is considered as structure-sensitive, hence, catalyst activity is a function of active components dispersion. Thereby, combination of promoter providing maximum stability with the palladium particles size providing maximum activity can lead to the obtaining of most efficient Pd-M/Al_2O_3 catalyst, which can effectively oxidize methane via staying relatively stable under reaction conditions.

The aim of this work was to study the influence of promoter type, effect of palladium particles size and the combination of these parameters on the supported palladium catalysts activity and tolerance to water vapor.

All kinetic studies were conducted under conditions of dry feed (CH_4:O_2:Ar = 1:5:94) and wet feed (CH_4:O_2:H_2O:Ar = 1:5:3:91) to reveal the effect of additional water in the initial reaction mixture. Also, temperature influence on the deactivation process was studied. It was shown that Ni and Co oxides additives led to the increase of activity, while Pt oxide additives not only greatly enhance the activity, but also increase the stability of palladium catalyst in comparison with unpromoted samples. The influence of promoter is higher at lower temperatures. The dependence of the unpromoted sample activity on the palladium dispersion was also studied in wet feed and dry feed.

As a result of these studies it is proposed that Pd-Pt/Al_2O_3 catalyst with Pd and Pt particles sizes of 8 and 4 nm respectively might be the most efficient catalyst for the unburned methane combustion.

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CONTENT

ABSTRACTS

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